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#11

13631-2  
I certify that this document and fee is being deposited on June 12, 2003 with the U.S. Postal Service as first class mail under 37 C.F.R. 1.8 and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

*Alayne Geller* ~~RECEIVED~~  
Alayne Geller  
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JUN 18 2003  
TC 1700

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

----- x  
In re Application of :  
Weihs *et al.* :  
: :  
Serial No.: 09/846,486 :  
: Group Art Unit: 1753  
Filed: 05/01/2001 : Examiner: S. Versteeg  
: :  
For: Freestanding Reactive Multilayer Foils :  
----- x

Honorable Commissioner of  
Patent and Trademarks  
Washington, D.C. 20231

**RECEIVED**

AUG 20 2003

**OFFICE OF PETITIONS**

PETITION UNDER 37 C.F.R. §1.181

REQUEST FOR REINSTATING FILING DATE

SIR:

Applicants hereby petition the Commissioner to reinstate the filing date of May 1, 2001 initially granted by the Office of Initial Patent Examination (OIPE) on June 27, 2001 and subsequently withdrawn by the same Office eight months later on February 13, 2002. An accompanying Notice of the OIPE (Exhibit A) alleges that the application was deposited without drawings and implies, without analysis, that a drawing is necessary for the understanding of the subject matter sought to be patented.

Applicants respectfully submit that the issue of the filing date was resolved months ago in favor of May 1, 2001. The OIPE had incorrectly treated this case as an application that could not be granted a filing date without drawings and sent a notice withdrawing the originally granted filing date of May 1, 2001. In response, applicants' attorney telephoned Ms. Robinson of the OIPE who referred him to the Office of Petitions. Applicants' attorney then telephoned the Office of Petitions using the number Ms. Robinson provided and discussed the problem with Ms. Gena Jones. A few days later Ms. Jones telephoned applicants' attorney and stated that a Notice of Omitted Item(s) would be issued and that the prior inconsistent notice from the OIPE would be withdrawn. This statement was noted in applicant's Preliminary Amendment, filed on April 12, 2002 (Exhibit B). However, the OIPE did not send a Notice of Omitted Item(s) or withdraw the prior inconsistent notice. Applicant's attorney then filed a Request For Corrected Filing Receipt (Exhibit C) on September 20, 2002 again requesting the OIPE to reinstate the May 1, 2001 filing date. OIPE did not respond until the May 15, 2003 denial (Exhibit A), which is the subject of this Petition.

Applicants respectfully petition on three grounds:

- I) The prosecution records of applicants' attorney indicate that the drawings were filed with the application text;
- II) Drawings are not necessary for understanding the subject matter sought to be patented; and
- III) Drawings useful in understanding the subject matter to be patented are incorporated by reference from the parent provisional application.

These grounds will be discussed in the order presented.

#### I. The Attorney's Records Indicate the Drawings Were Filed

While the nine month delay between applicants' May 1, 2001 filing and the February 13, 2002 withdrawal has dimmed specific recollection, the records of applicant's attorney indicate preparation of the drawings prior to May 1, 2001 and filing of the drawings with the application on May 1, 2001.

At the outset, applicants would emphasize that the present application claims the benefit of United States Provisional Application Serial No. 60/201,293 filed May 2, 2000 (Exhibit D). The Provisional Application closely parallels the present application in both text and drawings and was incorporated in the present application by reference (p. 1, lines 9-11). The most notable difference in text between the present application and Exhibit D is the addition in the present application of additional examples at pp. 17-19 and a five page recapitulation of the inventive features commencing at p. 19, line 13. This recapitulation describes nearly all embodiments subsequently claimed.

Exhibit E, taken from the attorney's prosecution file, is a copy of the six sheets of informal drawings believed filed with the present application on May 1, 2001. As can be seen, Figs. 1-4 correspond identically -- including reference numerals -- to Figs. 1-4, respectively, of the Provisional application (Exhibit D). Fig. 5 of the present application is the microphotograph as Fig. 6 of the Provisional. Thus Figs. 1-5 of the present application were prepared at least a year prior to the May 1 filing date.

Exhibit F is a copy of applicants' corresponding published PCT application filed May 2, 2001. A comparison shows that the PCT drawings are identical in substance to Exhibit E. This identity is consistent with preparation of the Exhibit E drawings from the May 1 filing date.

Exhibit G is a copy of applicants' letter of transmittal of the present application to the United States Patent and Trademark Office. The letter specifically refers to the inclusion of six sheets of drawings. Applicants' attorney here states that he signed the letter attached to the application to be sent and that it is his regular practice before signing such letters to check the application for inclusion of all items indicated in the letter including sheets of drawings.

Exhibit H is a copy of a USPTO Filing Receipt mailed June 27, 2001, Leasing Confirmation No. 7867, and granting the present application Serial No. 09/846,486 and a filing date of May 1, 2001. It is applicants' belief that the Office checks applications for completeness before mailing a Filing Receipt granting a serial number and filing date.

Exhibit I is a copy of a FAX transmission dated June 28, 2001 from JBL Patent Service Company to applicants' attorney transmitting formal patent drawings prepared from the informal

drawing of Exhibit E. These records are consistent with the belief of applicants' attorney -- confirmed by the Filing Receipt -- that the application with drawings had been filed in the USPTO on May 1, 2001.

II. Drawings Are Not Necessary For Understanding The Subject Matter Of This Invention

It is well established that inventive methods and inventive compositions are not readily subject to disclosure by drawing. Methods, for example, can be most clearly expressed in words. Consequently the presence of the word method in the title or claims has long excused the absence of a drawing.

In the present case, applicants' specification has an article title. Nonetheless it is primarily a method case. The application concludes with 43 claims. Of these, 32 are method claims (1-17, 22-28, 35-39 and 40-42), 4 are product-by-process claims (18, 29-31) and 7 are product claims. The method inventions are carefully described in words, the product-by-process claims are inherently described by the methods, and the handful of article claims are various forms of the articles depicted in Figs. 1 and 4, differing only by specified variation in composition or dimension.

The procedure applicable to patent applications filed with drawings omitted is set forth in MPEP § 601.01(f) and MPEP § 601.01(g). Applications containing method claims should not be denied the filing date of deposit even if the drawings are omitted.

MPEP 601.01(f) specifically notes that drawings are not required to obtain a filing date for applications containing method claims. It further provides that even if such application describes drawing figures but is filed the without drawings, the application should be treated as set forth in MPEP § 601.01(g), namely it should be granted the filing date of deposit and a Notice of Omitted Items should be sent.

The pertinent direction from MPEP 601.01(f) reads as follows:

A nonprovisional application having at least one claim...directed to the subject matter discussed above for which a drawing is usually not considered essential for a filing date, describing drawing figure(s) in the specification, but filed without drawings will be treated as an application without all of the drawing figures referred to in the specification as discussed in MPEP § 601.01(g), so long as the application contains something that can be construed as a written description.

The proper treatment of such an application as set forth in MPEP § 601.01(g) is the mailing of a Notice of Omitted Item(s) indicating that the application papers so deposited have been accorded a filing date, but are lacking some of the figures of drawings described in the specification.

In the present case, the application contains method claims. Specifically, it contains 32 method claims (1-17, 22, 28, 39 and 40-42). Furthermore it is abundantly clear that the application contains a written description. Indeed it contains 35 pages of written description including specific recitations of the methods claimed. See p. 19, line 13 *et seq.* Accordingly the application should be accorded the May 1, 2001 filing date.

### III. Useful Drawings Are Incorporated By Reference From The Provisional Application

Each invention claimed in the present application is described at least twice: once in a general description portion commencing at p. 5 and extending to the bottom of p. 16 and once in concise language analogous to claim language commencing at p. 19, line 13 and extending to p. 23. Some embodiments are described in a set of Examples at pp. 17-19. All drawings referred to in the general description from p. 5 to p. 16 are the same as Figs. 1-4 and 6 of the Provisional application (Exhibit D) that is the parent of the present application by reference. The drawings in the present case that are not in the Provisional (i.e. Figs. 6-9) are discussed only at pp. 17-19 in relation to four of the seven redundant examples and are not necessary to understanding any of the claimed subject matter.

Claim 1, the first independent claim, is on its face a “method of making a freestanding reactive multilayer foil.” It is concisely described at p. 19, lines 13-17:

It can now be seen that one aspect of the invention is a method of making a reactive multilayer foil composed of a plurality of alternating layers that can react exothermically. The method comprises the steps of providing a substrate, vapor depositing the alternating layers on the substrate to form the multilayer foil, and separating the multilayer foil from the substrate.

This method is earlier described as a method of making the foil 14 of Fig. 1. See p. 7, lines 18-23.

Claims 2-12 are all method claims dependent on claim 1. They are concisely described at p. 19 line 13 to p. 20, line 10. Each is described in as a method for making the foil of Fig. 1 or the foil used in Fig. 3:

<u>Claim</u>	<u>Exemplary Description</u>
2	P. 8, lines 1-7
3	P. 8, lines 10-16
4	P. 8, line 14
5	P. 8, lines 6-7
6	P. 20, lines 1-3
7	P. 20, lines 1-4
8	P. 7, lines 18-19
9	P. 7, lines 19-20
10	P. 9, lines 3-6
11	P. 13, lines 3-4

Claim 13, the next independent claim, is a method of bonding a first body to a second body using a reactive foil. The method in several variations is concisely described at p. 20, lines 11-18:

Another aspect of the invention is a method of bonding a first body to a second body comprising the steps of providing a freestanding reactive multilayer foil, pressing the bodies together against the foil and igniting the reactive foil. The ignited foil can melt material of the bodies or melt an associated meltable (joining material) layer to join the bodies together. Alternatively, the reaction product of the layers can itself be the joining material. One or both of the bodies can be semiconductor or microelectronic devices. The method is particularly advantageous for joining bodies having coefficients of thermal expansion, which differ by 1  $\mu\text{m}/\text{m}^{\circ}\text{C}$  or more.

The method of claim 13 is earlier described in relation to Figs. 2 and 3 at page 9 *et seq.*, as are its dependent method claims 14-17:

**Claim****Exemplary Description**

14

P. 14, lines 15-23; P. 15, lines 15-24

15

P. 12, line 2

16

P. 20, lines 17-18

17

P. 22, line 22 to P. 23, line 4

Claim 18 is the product made by the method of claim 13. Such a product is illustrated and described in relation to Fig. 5.

Claim 19, the third independent claim, is a product claim directed to a reactive multilayer foil. The invention of claim 19, as well as its dependent claims 20 and 21, are concisely described at p. 20, lines 19-23:

In an alternative embodiment, a reactive multilayer foil includes a plurality of openings through the thickness of the foil. The openings are preferably periodic over the foil area. These openings can be left unfilled or they can be filled with melttable materials, propellants, or other materials that will change or react on heating when the reactive foil is ignited.

These inventions are earlier illustrated and described in relation to Figs. 4 and 5 at p. 13, line 19 to p. 14, line 14 wherein a foil 14 has been provided with plural openings 22.

Independent claims 22, 23, 24 and 25 are directed to methods of making reactive foils provided with plural openings. These methods are concisely described at p. 21, lines 1-10:

Such apertured foils can be made by providing a substrate having a surface including a plurality of preformed openings, bumps or particles of thickness (or depth) comparable to or larger than the thickness of the multilayer foil to be deposited, depositing the reactive multilayer foil, and separating the resulting apertured multilayer foil from the substrate.

Alternatively, a reactive multilayer foil can be deposited on a substrate, patterned by a removable masking layer, and etched to form a plurality of holes. The apertured foil can then be removed from the substrate. Yet further in the alternative, a continuous foil can be formed and holes can be formed in the continuous foil by mechanical pressing.

Independent claim 26 and its dependent claims 27-28 are method claims directed to a bonding process using the foil having plural openings. These methods are concisely described at p. 21, lines 10-18:

The apertured foils have an important application in bonding. A reactive foil perforated by a plurality of openings is disposed between a first and a second body. If the body material is not melttable by the foil, a separate melttable layer or coating of

meltable joining material is also disposed between the bodies. The bodies are pressed together against the foil (and joining material) and the foil is ignited to melt joining material. The melted material flows within and through the openings in the foil to join the bodies. This approach produces a characteristic joint with ductility enhancing bridges through the openings. It is especially advantageous where one or both bodies are semiconductor or microelectronic devices or where the devices have CTEs that differ by more than  $1\mu\text{m}/\text{m}^{\circ}\text{C}$ .

Claims 29, 30, 31 claim products made by the methods of claims 26-28, respectively.

Claims 32, 34 and 35, which relate to embodiments illustrated in Figs. 6-9, will be discussed below.

Independent claim 33 is directed to a multilayer foil having a first set of reactive layers and a second set of reactive layers, wherein the layers of the first set are more reactive than the second. Such a structure, which would be similar in appearance to foil 14, is concisely described at p. 21, line 19 to p. 22, line 7.

Independent claim 40 is a method claim similar to claims 13 and 36 except it further calls for the disposition of a meltable joining material. The invention of claim 40 and its dependent claims 41 and 42 are described at p. 10, lines 7-17.

Independent claim 43 is an article claim reciting bodies bonded by specified joining region. Such a structure is described in relation to Figs. 4 and 5.

Thus the inventions of 39 of the 43 claims are clearly described with no reference whatsoever to the Figs. 6-9 added to the drawings of the parent Provisional application. The bulk of these claims are method claims which have been clearly described without reference to any drawings and also described in relation to drawings which are the same as those of the Provisional incorporated by reference.

Turning now to claims 32, 34 and 35 which relate to embodiments illustrated in Figs. 6-9, applicants respectfully submit that Figs. 6-9 are not necessary to understand the inventions of claims 32-35 and that, in any event, the descriptions of these embodiments are sufficiently clear

and complete that adequate drawings conforming to the specification can be prepared and submitted without introducing new matter.

Claim 32 is directed to a composite reactive foil comprising a first set of reactive layers and a second set of reactive layers and a second set of reactive layers wherein the layers of the first set are relatively thicker than those of the second set so that ignition of the second set ignites the first set.

While the claim 32 embodiment is illustrated in Fig. 7, the embodiment is concisely described without reference to Fig. 7 at p. 21, line 19 to p. 22, line 2:

A third type of novel reactive foil is a composite reactive multilayer foil in which the individual layers in the foil differ in thickness or in composition, on moving across the total thickness of the foil, to achieve advantageous results. One exemplary composite reactive multilayer foil comprises a first section with a plurality of relatively thick reactive layers, e.g. 1 $\mu$ m to 10 $\mu$ m, stacked on a second section with a plurality of thinner reactive layers (e.g. 1-1000 nm). The section with the thinner reactive layers ignites more rapidly than would the section with the thicker reactive layers. But as ignition spreads across the thinner section, it ignites the thicker section to produce a more uniform ignition and higher heat.

Given this clear exposition of the embodiment, the invention is readily understood. Moreover, given this description and the description of Fig. 7 provided at p. 17, lines 11-21, Fig. 7 can be submitted without adding new matter.

Similar considerations apply to the embodiment of claim 34 which is directed to a reactive multilayer foil having an area composed of two different regions, first regions where the layers can react to form an electrically conductive material and second regions where the layers can react to form non-conductive material.

While the claim 34 embodiment is illustrated in Figs. 9A and 9B (before reaction and after), the embodiment is concisely described without reference to Figs. 9 at p. 22, lines 8-16:

A fourth type of novel reactive foil has a major surface area composed of at least two different regions: one or more first regions which will react to form electrically conductive material and one or more second regions which are non-conductive. Such foils are particularly useful in connecting semiconductor device electrical contacts to a substrate having receiving contacts. A foil can be disposed between the device and the substrate with the device contacts, the contacts of the substrate and the first regions of the foil all in registration. The device and substrate are then pressed against the foil, and the foil is ignited to bond the device to the substrate with the respective contacts conductively connected and the other regions non-conductively bonded.

In view of this description, the invention of claim 34 is readily understood. And in view of this description and the description of Figs. 9A and 9B provided at p. 19, lines 4-9, Figs. 9A and 9B can be submitted without adding new matter.

In view of the foregoing, it is submitted that contemporaneous documents and actions corroborate the statement in applicants' letter of transmittal that the six sheets of drawings in Exhibit D were included with the application filed May 1, 2001. Applicants had prepared the drawings; the drawings were accurately described in the specification; and the drawings were referred to in the letter of transmittal. The very next day on May 2, 2001, copies of the same drawings were filed with a corresponding PCT application. Shortly after the filing, the Office mailed a Filing Receipt granting a serial number and filing date and applicants' attorney ordered and received corresponding formal drawings from a draftsman. Nothing inconsistent with the normal filing of a complete application occurred until nine months after the filing date when the OIPE abruptly withdrew its grant of a filing date alleging for the first time that the application was incomplete because it had no drawings and asserting, without analysis, that drawings are necessary to understand the inventions. Applicants respectfully submit that this process is unfair, undermines reasonable reliance on notices issued by the Office and is inconsistent with the evidence of record.

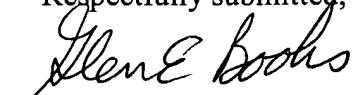
The assertion that the drawings are necessary to understand the inventions claimed in this application is also without foundation. As demonstrated above, the bulk of the claims are method claims which normally do not require drawings. It is correct that applicants chose to

schematically illustrate products, components and processing arrangements to assist in the description of the inventions, but the principal illustrations used were Figs. 1-4 and 6 of the parent Provisional application which the present application claims the benefit of and incorporates by reference. These drawings are not only similarly described in the parent Provisional but also correspond even in the reference numerals to Figs. 1-4 of the present case. The Detailed Description of the present application proceeds from page 5 to page 16 without reference to any drawing other than Figures corresponding to Figs. 1-4 and 6 of the parent Provisional. The only new figures added to those previously put in the Provisional are Figs. 6-9 which are discussed only in the context of additional illustrative Examples at pp. 17-19.

In addition, at the end of the application applicants concisely described each and every feature of the inventions they would subsequently claim without reference to any drawings. Accordingly it is submitted that the drawings were filed with the application. If they were not, the inventions claimed can be understood without the drawings, especially in view of the incorporation by reference of the parent Provisional application which contains nearly identical drawings and nearly identical descriptions.

Please charge the petition fee of \$130 to Deposit Account No. 501358. The Commissioner is hereby authorized to charge any deficiencies or credit any overpayment to Deposit Account No. 501358. A duplicate copy of this sheet is enclosed.

Respectfully submitted,



Glen E. Books  
Reg. No. 24,950  
Attorney for Applicants

DATED: June 12, 2003

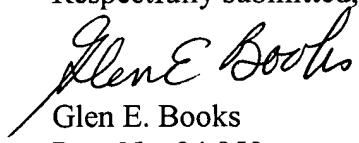
LOWENSTEIN SANDLER PC  
65 Livingston Avenue  
Roseland, NJ 07068  
Tel.: 973-597-6162

schematically illustrate products, components and processing arrangements to assist in the description of the inventions, but the principal illustrations used were Figs. 1-4 and 6 of the parent Provisional application which the present application claims the benefit of and incorporates by reference. These drawings are not only similarly described in the parent Provisional but also correspond even in the reference numerals to Figs. 1-4 of the present case. The Detailed Description of the present application proceeds from page 5 to page 16 without reference to any drawing other than Figures corresponding to Figs. 1-4 and 6 of the parent Provisional. The only new figures added to those previously put in the Provisional are Figs. 6-9 which are discussed only in the context of additional illustrative Examples at pp. 17-19.

In addition, at the end of the application applicants concisely described each and every feature of the inventions they would subsequently claim without reference to any drawings. Accordingly it is submitted that the drawings were filed with the application. If they were not, the inventions claimed can be understood without the drawings, especially in view of the incorporation by reference of the parent Provisional application which contains nearly identical drawings and nearly identical descriptions.

Please charge the petition fee of \$130 to Deposit Account No. 501358. The Commissioner is hereby authorized to charge any deficiencies or credit any overpayment to Deposit Account No. 501358. A duplicate copy of this sheet is enclosed.

Respectfully submitted,



Glen E. Books  
Reg. No. 24,950  
Attorney for Applicants

DATED: June 12, 2003

LOWENSTEIN SANDLER PC  
65 Livingston Avenue  
Roseland, NJ 07068  
Tel.: 973-597-6162

Exhibit A



# UNITED STATES PATENT AND TRADEMARK OFFICE

COMMISSIONER FOR PATENTS  
UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, DC 20231  
www.uspto.gov

APPLICATION NUMBER	FILING DATE	FIRST NAMED APPLICANT	ATTY DOCKET NO./TITLE
09/846,486	04/18/2002	Timothy P. Weihns	13631-2A

CONFIRMATION NO. 786



\*OC000000010048537\*

GLEN E. BOOKS, ESQ.  
LOWENSTEIN SANDLER PC  
65 LIVINGSTON AVENUE  
ROSELAND, NJ 07068

RECEIVED  
JUN 18 2003  
TC 1700

Date Mailed: 05/15/2003

## RESPONSE TO REQUEST FOR CORRECTED FILING RECEIPT

### Application Filing Date

In response to your request for a corrected Filing Receipt, the Office can not comply with your request because:

- If your application was submitted under 37 CFR 1.10, your filing date should be the "date in" found on the Express Mail label. If there is a discrepancy, a petition to accord a filing date should be submitted along with a copy of the Express Mail label showing the "date in" and be directed to the Office of Petitions.
- A copy of the Express Mail label was not enclosed with your request. Petitions under 37 CFR 1.10 require a copy of the Express Mail Label to be submitted.
- The "date in" on the Express Mail label is the date given on the Filing Receipt.
- The filing date accorded to the application is the date the application met the filing date requirements of 37 CFR 1.53(b) or (c).**

Applications submitted with a certificate of mailing under 37 CFR 1.8 are accorded a filing date as of the date the application is received in the U.S. Patent and Trademark Office. A request to review the filing date accorded to the application must be in the form of a petition.

The filing date on your return postcard is the same as the date on your Filing Receipt. A request to review the filing date accorded to the application must be in the form of a petition.

A petition under 37 CFR 1.10, 37 CFR 1.53 or 37 CFR 1.182 is needed to request a change to the filing date. A \$130 petition fee is required for a petition under 1.53 or 1.182. If you choose to file a petition, the petition and the \$130 petition fee, if any, to:

Box DAC  
Commissioner for Patents  
Washington, DC 20231

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M. S.  
Customer Service Center  
Initial Patent Examination Division  
(703) 308-1202

Exhibit B

I certify that this document and fee is being deposited on April 12, 2002 with the U.S. Postal Service as first class mail under 37 C.F.R. 1.8 and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

  
Alayne Geller

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

----- x  
In re Application of :  
Weihs *et al.* :  
Serial No.: 09/846,486 :  
Filed: 05/01/2001 : Group Art Unit: 1775  
For: Freestanding Reactive Multilayer Foils : Examiner: TBA  
----- x

Honorable Commissioner of  
Patent and Trademarks  
Washington, D.C. 20231

SIR:

**PRELIMINARY AMENDMENT**

Please enter in the above-identified case the six sheets of formal drawings enclosed herewith. Applicants have been informed by Ms. Gena Jones of the Office of Petitions that a Notice of Omitted Item(s) will be issued in this case and that prior inconsistent notices from the OIPE will be withdrawn.

The drawings are not new matter. Figures 1, 2, 3, 4 and 5 are contained in the parent U.S. Provisional Application Serial No. 60/201,293 which is incorporated in this case by reference. The remaining Figures conform to detailed descriptions of specific examples set forth at pp. 17-19 of the specification. They are helpful but not necessary for understanding the inventions

claimed herein

Respectfully submitted,

*Glen E. Books*  
Glen E. Books  
Reg. No. 24,950  
Attorney for Applicants

DATED: April 12, 2002

LOWENSTEIN SANDLER PC  
65 Livingston Avenue  
Roseland, NJ 07068  
Tel.: 973-597-6162

*freestanding Reactive*  
TITLE/MARK: multi-layer foils

CASE NO.: 13631-2

SERIAL NO.: 09/846,486

The Patent and Trademark Office acknowledges, and has stamped hereon, the date of the receipt of the items checked below and acknowledges authority to charge all fees to Account '501358

PATENT APPLICATION • COMPLETE WITH:

FEE AUTHORITY (x2)  CHECK

PRIORITY DOCUMENT

6 SHEETS OF (IN) FORMAL DRAWINGS

DECLARATION & POWER OF ATTORNEY

EXPRESS MAIL CERT. # \_\_\_\_\_

SMALL ENTITY STATEMENT

AMENDMENT  ASSIGNMENT  CHECK  APPEAL NOTICE

APPEAL BRIEF  LETTER  PETITION

PRELIMINARY STATEMENT  PRIOR ART STATEMENT

STIPULATION  EXTENSION OF TIME

NOTICE OF OPPOSITION

ISSUE FEES:  BASE ISSUE  SUPPLEMENTAL

CERTIFICATE OF CORRECTION

DECLARATION

TRADEMARK APPLICATION • COMPLETE WITH:

FEE AUTHORITY  CHECK

DRAWING  SPECIMEN

COPYRIGHT APPLICATION • COMPLETE WITH:

TRANSMITTAL LETTER

CHECK

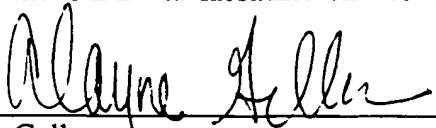
DEPOSIT COPIES

*4/12/02*



Exhibit C

I certify that this document and fee is being deposited on September 20, 2002 with the U.S. Postal Service as first class mail under 37 C.F.R. 1.8 and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231: Attention Office of Initial Patent Examination (OIPE); the document has also been sent to the OIPE via facsimile on 703-746-9195.

  
Alayne Geller

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

----- x  
In re Application of :  
Weihs *et al.* :  
: :  
Serial No.: 09/846,486 :  
: : Group Art Unit: 1775  
Filed: 05/01/2001 : : Examiner: TBA  
: :  
For: Freestanding Reactive Multilayer Foils :  
----- x

Honorable Commissioner of  
Patent and Trademarks  
Washington, D.C. 20231

SIR:

**REQUEST FOR CORRECTED FILING RECEIPT**

Applicants respectfully request a corrected filing receipt. The attached filing receipt mailed August 29, 2002 states the filing date as April 18, 2002 corresponding to applicants' filing of formal drawings rather than the filing date of May 1, 2001 corresponding to applicants' deposit of the application with drawings allegedly omitted.\*

It is believed that the OIPE continues to treat this application as one that requires drawings to receive a filing date. To the contrary, the application contains method claims and

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\*Applicants use the term "allegedly omitted" because the application incorporated by reference the parent provisional application which included most of the referenced drawings.

accordingly does not require drawings in order to receive a filing date. The application is therefore entitled to the filing date of deposit (May 1, 2001) even if the drawings were omitted (MPEP § 601.01(f) and § 601.01(g)).

Applicants respectfully submit that the issue of the filing date was resolved months ago in favor of May 1, 2001. The OIPE had incorrectly treated this case as an application that could not be granted a filing date without drawings and sent a notice withdrawing the originally granted filing date of May 1, 2001. In response, applicants' attorney telephoned Ms. Robinson of the OIPE who referred him to the Office of Petitions. Applicants' attorney then telephone the Office of Petitions using the number Ms. Robinson provided and discussed the problem with Ms. Gena Jones. A few days later Ms. Jones telephoned applicants' attorney and stated that a Notice of Omitted Item(s) would be issued and that the prior inconsistent notice from the OIPE would be withdrawn. This statement was noted in applicant's Preliminary Amendment, filed on April 12, 2002. But the OIPE has not yet sent the Notice of Omitted Item(s) nor withdrawn the inconsistent Notice of Withdrawal.

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The pertinent direction from MPEP 601.01(f) reads as follows:

A nonprovisional application having at least one claim...directed to the subject matter discussed above for which a drawing is usually not considered essential for a filing date, describing drawing figure(s) in the specification, but filed without drawings will be treated as an application without all of the drawing figures referred to in the specification as discussed in MPEP § 601.01(g), so long as the application contains something that can be construed as a written description.

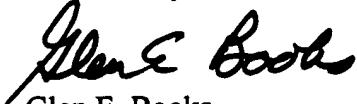
The proper treatment of such an application as set forth in MPEP § 601.01(g) is the mailing of a 'Notice of Omitted Item(s) indicating that the application papers so deposited have been accorded a filing date, but are lacking some of the figures of drawings described in the specification.

In the present case, the application contains method claims. Specifically, it contains 32 method claims (1-17, 22, 28, 39 and 40-42). Furthermore it is abundantly clear that the application contains a written description. Indeed it contains 35 pages of written description including specific recitations of the methods claimed. See p. 19, line 13 *et seq.* Accordingly the application should be accorded the May 1, 2001 filing date.

In view of the foregoing, applicants respectfully request the mailing of the appropriate Notice of Omitted Item(s), withdrawal of the prior inconsistent Notice, and correction of the filing receipt mailed August 29, 2002.

No fee is believed required for entry of this Request; if any fee is due however, please charge the required fee or credit any overpayment to deposit account number 501358.

Respectfully submitted,

  
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Reg. No. 24,950  
Attorney for Applicants

DATED: September 20, 2002

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standing Reactive multi layer  
TITLE/MARK: toile

CASE NO.: 13631-2

SERIAL NO.: 09/846,486

The Patent and Trademark Office acknowledges, and has stamped hereon, the date of the receipt of the items checked below and acknowledges authority to charge all fees to Account \*501358

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Patent  
Docket No.: J5450.0024/P024

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR U.S. LETTERS PATENT

Title:

REACTIVE MULTILAYER FOILS

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## REACTIVE MULTILAYER FOILS

Government Interest: This invention was made with government support under Grant Nos. DMR 9702546, DMR 9632526, awarded by the National Science Foundation, and DAAL 019620047, awarded by the Army Research Laboratory. The government has certain rights in the invention.

### BACKGROUND OF THE INVENTION

In almost every industry involving the joining of materials, improvements in bonding become important as the technologies of those industries advance. This is especially true as the materials to be bonded become increasingly smaller in scale and 10 increasingly delicate in form and function. Additionally, the development and use of new materials with characteristics that make them difficult to bond have presented many problems to industry and science.

In many methods of bonding or joining materials, a heat source is required. 15 This heat source may either be external or internal to the structure to be joined. When external, the heat may be generated from a device such as a furnace. Processes incorporating such heat sources require the heating of the entire unit to be bonded, including the bulk materials and the bond material (e.g., any braze or solder material), to a temperature high enough to melt that bond material or the bulk material itself. 20 Such a method presents problems because the bulk materials desired to be joined are often delicate or sensitive to the high temperatures required of the process. These high temperatures required for joining, or mismatches in thermal contractions on cooling, may damage the materials to be bonded.

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To alleviate the problems associated with external heat sources, internal heat sources are utilized. These heat sources often take the form of reactive powders or even electrical wires. When reactive powders are used, the powders will be made up of a mixture of metals or compounds that will react exothermically to form a final compound or alloy. Such processes have existed since the exothermic reactions of powders were developed in the early 1960s, spawning what is known as Self-Propagating, High-Temperature Synthesis (SHS). The properties of SHS reactions such as energy released or diffusion of the energy, however, are often difficult to control. As a result, bonding may be inconsistent or insufficient.

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10 To combat the problems associated with reactive powder bonding, multilayer structures composed of materials which allow similar exothermic reactions have been developed. Such structures allow for reactions with more controllable and consistent heat generation. The basic driving force behind such exothermic reactions is a reduction in atomic bond energy. When a structure having a series of layers of reactive material (known as a "foil") is ignited, heat is produced locally as the distinct layers mix atomically. This heat ignites adjacent regions of the foil, thereby allowing the reaction to travel the entire length of the structure, generating heat until all material is reacted. Even with such advances in bonding technology, however, there remain problems. Many materials, for example, pose major difficulties in joining and previously could not 15 be bonded successfully. Additionally, methods utilizing reactive foils as heat sources often resulted in the foils debonding from their substrates upon reaction, thereby weakening the bond. Another drawback of the known technology is that current 20

reactive foils must be adhered to the materials desired to be joined, and as a result the versatility of known joining methods is severely reduced.

#### SUMMARY OF THE INVENTION

Reactive foils are used as localized heat sources. The reactive foil is preferably a freestanding multilayered foil structure made up of alternating layers selected from materials that will react with one another in an exothermic and self-propagating reaction. Upon reacting, this foil supplies highly localized heat energy that may be applied, for example, to joining layers, or directly to bulk materials that are to be joined. This foil heat-source allows rapid bonding to occur at room temperature in many environments (e.g., air, vacuum, Argon, water, etc.). If a joining material is used, the foil reaction will supply enough heat to melt the joining materials, which upon cooling will form a strong bond, joining two or more bulk materials. If no joining material is used, the foil reaction supplies heat directly to at least two bulk materials, melting a portion of each bulk, which upon cooling, form a strong bond. Additionally, the foil may be designed with openings (e.g., perforations, cracks, etc.) that allow extrusion of the joining (or bulk) material through the foil to enhance bonding of materials or the objects/things (e.g., electronic chips, microdevices, etc.) in which they are embodied.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Many advantages, features, and applications of the invention will be apparent from the following detailed description of preferred embodiments of the invention, which is provided in connection with the accompanying drawings, in which:

Fig. 1 illustrates an exemplary multilayer reactive foil in accordance with a preferred embodiment of the invention;

Fig. 2 illustrates freestanding elements of an exemplary joining application in accordance with a preferred embodiment of the invention;

5 Fig. 3 illustrates initiation of a self-propagating, exothermic reaction in accordance with a preferred embodiment of the invention;

Fig. 4 illustrates an exemplary perforated reactive foil in accordance with a preferred embodiment of the invention;

10 Fig. 5 illustrates an exemplary cracked reactive foil in accordance with a preferred embodiment of the invention; and

Fig. 6 illustrates extrusion of joining material through openings in a reactive foil in accordance with a preferred embodiment of the invention.

#### DETAILED DESCRIPTION

Preferred embodiments and applications of the invention will now be described. Other embodiments may be realized and compositional or structural changes may be made to the disclosed embodiments without departing from the spirit or scope of the invention. Although the preferred embodiments disclosed herein have been particularly described as the generation of an intense localized heat source utilizing a freestanding, self-propagating reactive foil structure as applied to joining bulk materials, it should be readily apparent that the invention may be embodied for any use or application having the same or similar problems.

In accordance with a preferred embodiment of the invention, a multilayer reactive structure (generically referred to herein as a "foil") is provided as a local heat source in a variety of applications such as a process for joining two or more (of the same or different) materials together. As illustrated in Fig. 1, reactive multilayer foil 14 is made up of alternating layers 16 and 18 of materials A and B, respectively. These alternating layers 16 and 18 may be any materials amenable to mixing of neighboring atoms (or having changes in chemical bonding) in response to a stimulus. These reactants may be chosen so as to form silicides (e.g., Rh/Si, Ni/Si, and Zr/Si, etc.), aluminides (e.g., Ni/Al, Ti/Al, Monel/Al, and Zr/Al, etc.), borides, carbides (e.g., Ti/C), thermite reacting compounds (e.g., Al/Fe<sub>2</sub>O<sub>3</sub> or Al/Cu<sub>2</sub>O), alloys, metallic glasses, and composites (e.g., metal ceramic).

The materials (A/B) used in formation of the reactive foil are preferably chemically distinct. In a preferred embodiment, layers 16, 18 alternate between a transition metal (e.g., Ti, Ni, etc.) and a light element (e.g., B, Al, etc.). Preferably, the pairs (A/B) of elements are chosen based on the way they react to form stable compounds with large negative heats of formation and high adiabatic reaction temperatures, as described in Weihs, "F7 "Self-Propagating Reactions in Multilayer Materials," Handbook of Thin Film Process Technology, 1997, which is incorporated herein by reference in its entirety. In a preferred embodiment, at least one of the layers of the reactive foil is (or contains) Al.

When one end of a multilayer foil 14 is exposed to a stimulus (e.g., spark, energy pulse, etc.), for example, neighboring atoms from materials A and B mix, as shown in Fig. 1. The change in chemical bonding caused by this mixing results in a

reduction in atomic bond energy, thus generating heat in an exothermic chemical reaction. This chemical reaction occurs as layers with **A-A** bonds (i.e., layer 16) and layers with **B-B** bonds (i.e., layer 18) are exchanged for **A-B** bonds, thereby reducing the chemical energy stored in each layer, and generating heat. As Fig. 1 further illustrates, this generated heat diffuses through foil 14 (in a direction from reacted section 30 through reaction zone 32 to unreacted section 34) and initiates additional mixing of the unreacted layers. As a result, a self-sustaining/self propagating reaction is produced through foil 14. With sufficiently large and rapid heat generation, the reaction propagates across the entire foil 14 at velocities greater than 10 m/s. As the reaction does not require additional atoms from the surrounding environment (for example, oxygen in the case of combustion), the reaction makes foil 14 a self-contained source of energy capable of a rapid burst of heat, reaching temperatures above 1400 K, and a local heating rate reaching  $10^9$  K/s. This energy is particularly useful in applications (e.g., joining, ignition, etc.) requiring production of heat rapidly and locally.

When a reaction propagates along a multilayer foil 14 as illustrated by Fig. 1, the maximum temperature of the reaction is typically located at the trailing edge of the reaction zone 32. This may be considered the final temperature of reaction which can be determined by the heat of reaction ( $\Delta H_r$ ), the heat lost to the environment ( $\Delta H_{env}$ ), and the average heat capacity of the sample ( $C_p$ ). Another factor is whether or not reaction temperature exceeds the melting point of the final product. If the melting point is exceeded, then some heat is absorbed in the state transformation of the product from solid to liquid. The final temperature of reaction may be determined using the

following formulas (where  $T_o$  is the initial temperature,  $\Delta H_m$  is the enthalpy of melting, and  $T_m$  is the melting temperature), depending upon whether final product melting occurs:

$$T_f = T_o - (\Delta H_{rx} + \Delta H_{env}) / (C_p M) \quad \text{If no melting of final product occurs;}$$

5       $T_f = T_m$       If there is a two-phase region of solid and liquid final product; and

$$T_f = T_o - (\Delta H_{rx} + \Delta H_{env} + \Delta H_m) / (C_p M) \quad \text{If the final product completely melts.}$$

Intricately related to the heat of the foil reaction is the velocity of the propagation of the reaction along the length of foil 14. The speed at which the reaction can propagate may depend on how rapidly the atoms diffuse normal to their 10 layering (Fig. 1) and how rapidly heat is conducted along the length of foil 14. The propagation velocity is a strong function of the foil's multilayer thickness. As the thickness of individual layers 16, 18 decreases, the diffusion distances are smaller and atoms can mix more rapidly. Heat is released at a higher rate, therefore, and the reaction travels faster through the foil structure.

15      In accordance with a preferred embodiment of the invention, reactive multilayer foils 14 may be fabricated by physical vapor deposition (PVD) methods. A magnetron sputtering technique, for example, may be used to deposit the materials A/B on a substrate (shown in Fig. 1 in dashed outline form as layer 35) as alternating layers 16, 18. Substrate 35 may be rotated over two sputter guns in a manner well known in the art to effectuate the layering of materials A/B into alternating layers 16,

18. With this method, each pass over a source generates an individual layer in a controlled manner.

Substrate 35 is shown in dashed outline form to indicate that it is a removable layer that facilitates fabrication of the reactive foil 14 as a free-standing foil.

5 Substrate 35 may be any substrate (e.g., Si, glass, or other underlayer) having the characteristics of providing sufficient adhesion so as to keep the foil layers on the substrate during deposition, but not too adhesive to prevent the foil from being safely, easily, and adequately removed from the substrate following deposition.

In accordance with a preferred embodiment, an additional adhesion or 10 release layer (e.g., tin) may be used as an interface layer between the first layer of foil (16 or 18) and the substrate 35 to provide the necessary adhesion. When no adhesion layer is employed, selection of the appropriate material A/B as the first layer deposited on the substrate will ensure that the necessary adhesive requirements are met. When a reactive foil using Al/Monel as materials A/B is to be fabricated, for example, without 15 an adhesion layer, the exemplary reactive foil would be deposited on a substrate such as Si with the first layer being Al deposited on the substrate. Al is preferably selected as the first layer in such case because Al will sufficiently adhere to Si during depositing, but will allow peeling off of the substrate after the foil is formed.

In an alternative embodiment, the foil is deposited by first forming a 20 sacrificial layer on the substrate, before the foil's multilayers are deposited. After the foil is formed, the foil is subsequently removed from the substrate utilizing techniques such

as chemical attack upon the sacrificial layer. Examples of sacrificial layers include copper (which is attacked using nitric acid) or a photoresist layer (which may be attacked by an appropriate organic solvent). Any known sacrificial layer and corresponding removal technique may be utilized, however, in reducing the invention to practice.

5       A fabricated foil 14 may have hundreds to thousands of alternating layers 16 and 18 stacked on one another. Individual layers 16 and 18 preferably have a thickness ranging from 1-10,000 nm. In a preferred embodiment, the total thickness of foil 14 may range from 1  $\mu$ m to 1 cm.

10       Another preferred method of fabricating is to deposit material in a codeposition geometry. Using this method, both material sources are directed onto one substrate and the atomic fluxes from each material source are shuttered to deposit the alternate layers 16 and 18.

15       In accordance with a preferred embodiment, the degree of atomic intermixing of materials A/B that may occur during deposition should be minimized. This may be accomplished by depositing the multilayers onto cooled substrates, particularly when multilayers 16 and 18 are sputter deposited. To the extent some degree of intermixing is unavoidable, a relatively thin (as compared to the alternating unreacted layers) region of pre-reacted material 20 will be formed. Such a pre-reacted region 20, nevertheless, is helpful in that it serves to prevent further and spontaneous 20 reaction in foil 14 during deposition and removal.

In accordance with another preferred embodiment, a multilayer reactive foil may be fabricated using mechanical techniques such as repeated rolling of layered composites.

As illustrated in Fig. 2, the reactive foil 14 resulting from fabrication in accordance with a preferred embodiment of the invention is a freestanding multilayer reactive foil for particular use as a heat generating source. Freestanding foils in accordance with a preferred embodiment are easier to characterize than thin films because they can be handled like "bulk" samples. Making reactive foils 14 freestanding in accordance with a preferred embodiment greatly expands their possible uses. Because such reactive foils are not necessarily associated with any particular application they may be mass produced for any purpose requiring a self-propagating localized heat source. Moreover, freestanding foils in accordance with a preferred embodiment will allow heat sinking to the substrate to be minimized where unwanted.

Freestanding foils in accordance with preferred embodiments of the invention may be adapted for use in a variety of applications. In accordance with one preferred embodiment of the invention, for example, the freestanding foils may be used to join, bond, or otherwise couple materials (generically referred to herein as "bulk materials") together to form a unified product. Freestanding foils in accordance with the invention may find use in any number of joining applications (e.g., bonding, soldering, brazing, welding or other forms of similar applications) to couple or otherwise join bulk materials (and the objects, things, devices, or components in which they are embodied). A typical joining application is represented in Fig. 2, in which two or more bulk materials 10 are to be joined together. In accordance with a preferred

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embodiment, bulk materials 10 may be ceramics, metallic glasses, metals/alloys, polymers, composites, semiconductors, and other forms of materials and components.

In the particular joining application illustrated in Fig. 2, joining materials 12 are to be used to join bulk materials 10 together. Joining material 12 may be any layer (or composite layer) of material to be melted to join bulk materials 10 together. In accordance with a preferred embodiment, joining material 12 is in the form of freestanding sheets made up of metallic glasses, metals/alloys, functionally graded layers, Ni-B films, self-propagating brazes, combinations of such, or other like joining materials such as commercial brazes or solders.

10 In accordance with a preferred embodiment of the invention, a reactive foil  
14 is positioned between joining materials 12 to form a structure somewhat like a  
sandwich. The reactive foil "sandwich" thus formed is preferably positioned between  
bulk materials 10 at the location (e.g., end point, joint, intersection, etc.) at which the  
bulk materials 10 are to be joined together, as shown in Fig. 2.

15 In accordance with a preferred embodiment, the joining process involves the application of a force, preferably, perpendicular to the joint to be formed (as symbolically represented by vice 11) to maintain the relative positions of bulk materials 10, joining materials 12, and reactive foil 14, as shown in Fig. 3. In a preferred embodiment, all components are freestanding elements presented together. In an alternative embodiment, joining materials 12 are presented as a composite with reactive foil 14.

Once the components of the joining process are positioned, a stimulus (shown in Fig. 3 as lighted match 15) is applied, preferably, to one end of reactive foil 14 to initiate a self-propagating reaction in the foil. As described above, during the SHS reaction, the intermixing of atoms within reactive foil 14 produces rapid and intense heat sufficient to melt joining materials 12 along the entire length of reactive foil 14. In this state, joining materials 12 are sufficient to join bulk materials 10 together. Shortly thereafter, the joined materials 10 return to the temperature of the environment (e.g., room temperature) and can be removed from the applied force (i.e., graphically represented by vice 11).

10 In accordance with a preferred embodiment, a composite structure composed of joining materials 12 and reactive foil 14 is formed through deposition (e.g., vapor depositing) of reactive foil 14 onto one layer of joining material 12. Another layer of joining material is then combined with reactive foil 14 through an application of force (e.g., cold rolling) on the second layer of joining material 12 to adhere to reactive foil 15 14.

In accordance with a preferred embodiment of the invention, a joining application can take the form of a welding process (e.g., joining metallic glasses together without a braze layer), whereby the reaction locally melts the surface of the bulk materials to be joined without use of any joining material (e.g., braze). This process facilitates ease of joining and may result in a stronger joint than other non-welding applications. Furthermore, as sections of the bulk material melt and penetrate openings in the foil, there are likely to be less thermal stresses present.

In accordance with a preferred embodiment of the invention, all components to the joining process, including the foil, the joining material, and the bulk materials, are free-standing. Such an embodiment facilitates ease of fabrication or set-up. Furthermore, it is relatively easy to change the joining material and foil combinations or 5 relative thickness.

In accordance with a preferred embodiment of the invention, the reactive foil may have a layer of joining material (e.g., braze) combined with the reactive foil. A number of different techniques may be utilized to such as directly depositing (e.g., by vapor deposition or electrodeposition) the joining material on the foil, cold-rolling the 10 joining material on the foil, as well as dipping the foil into molten joining material. In such an embodiment, only a single component need be positioned between the materials to be joined, thereby easing set-up. In such an embodiment, the foil 14 is 15 easily handled, more stable, and mechanically robust.

In accordance with a preferred embodiment of the invention, bulk material may be pre-wet with joining material. In such an embodiment, the reactive foil will melt the outer sections of the joining material, which then joins directly to the foil. The bulk material will be subjected to less heat from the foil than in alternative geometries because the foil only has to melt a surface immediately adjacent to the foil. By utilizing such an embodiment, it is possible to join a broader range of bulk materials.

20 In accordance with a preferred embodiment of the invention, a wetting/adhesion layer may be added to facilitate surface wetting for the reactive foil 14, bulk materials 10, or both. The wetting/adhesion layer allows uniform spreading

of joining material to ensure consistent joining of bulk materials. In accordance with a preferred embodiment, the wetting/adhesion layer may be a thin layer of joining material (e.g., braze), Ti, Cr, Sn, metallic glass, etc. Commercial alloys such as Ag-Sn, Ag-Cu-Ti, Cu-Ti, Au-Sn, and Ni-B may also be used.

5 Preferred embodiments of the invention are useable as freestanding reactive foils with increased total thicknesses. The total thickness of such a reactive foil depends upon the thickness and number of the elemental layers (e.g., 16 and 18) utilized to form the foils. Foils that are less than 10  $\mu\text{m}$  are very hard to handle as they tend to curl up on themselves. Foils on the order of 100  $\mu\text{m}$  are stiff, and thus, easily handled.

10 Thicker foils also reduce the chance of quenching. In joining applications using reactive foils, there is a critical balance between the rate at which the foil generates heat and the rate at which that heat is conducted into the surrounding braze layers and the joint to be formed. If heat is conducted away faster than it is generated, the reaction will be quenched and the joint cannot be formed. The thicker foils make it harder to quench the reaction because there is a larger volume generating heat and the same surface area through which heat is lost.

15

Thicker foils can be utilized with reaction temperatures that are lower, generally leading to more stable foils. Foils that are unstable or brittle are dangerous and difficult to use. Brittle foils, for example, will crack easily leading to local hot spots (through the release of elastic strain energy and friction) that can ignite the foil. Cutting such brittle foils (e.g., for specific joint sizes) is very difficult to do as they are more likely to crack into unusable pieces or ignite during the cutting process.

20 Freestanding thick foils offer the advantage of overcoming problems associated with

thermal shock (coefficient of thermal expansion (CTE) mismatch, and densification) problems that have presented obstacles in known processes. The thermal shock, CTE mismatch has caused thinner foils that are deposited on substrates to debond during reaction, thereby causing inconsistent and less effective bonding. By making the foil 5 freestanding in accordance with a preferred embodiment of the invention, no debonding occurs, the foil is easily manipulated and handled, and thus the reactive foil is made available to a greater variety of applications.

In accordance with a preferred embodiment, the thicker reactive foils are on the order of 50-200  $\mu\text{m}$  for nanolaminates. Although a number of different systems 10 may be employed to create the thick, freestanding reactive foils, a unique process in selecting the fabrication conditions for the employed system must be undertaken. In accordance with a preferred embodiment, for example, sputter deposition, deposition conditions such as sputter gas pressure and substrate temperature must be chosen to produce the lowest stresses in the layers of the films of the foil as they are deposited in 15 the system. Stresses often arise in the films during the fabrication process. As the films grow thicker, they are more likely to peel off their substrates or crack their substrates than thinner films, thereby ruining the foil production. By characterizing the stresses in the films and selecting conditions to minimize the stresses, the fabrication process can be completed without the peeling off (or cracking) of the substrate.

20 In accordance with a preferred embodiment of the invention, openings in a reactive foil are intentionally designed or patterned into the foil. These openings are of particular use in facilitating and enhancing joining applications.

The foil may be initially fabricated, for example, with one or more perforations 22 through the foil structure, as shown in Fig. 4. Any known method may be employed to create openings 22. For example, sputter depositing of the foil 14 on a removable substrate with patterned holes may be used. The openings may also be 5 formed by depositing the foil 14 onto a substrate, coating with photoresist, patterning holes 22 into the photoresist, and subsequently etching holes 22 into the foil 14. A further exemplary technique involves physically punching holes in foil 14 compositions.

As shown in Fig. 4 and Fig. 6, the openings in foil 14 allow joining material 12, or bulk material 10 in some circumstances, to extrude (as shown by arrows 26) 10 through these perforations 22 upon being heated and melted by the exothermic reaction of foil 14. Upon this extrusion, one layer of joining material 12, or bulk material 10, may contact and couple with another layer 12, or bulk material 10, on the opposite side of the freestanding foil 14. The patterned perforations 22 allow for 15 enhanced bonding of bulk materials 10 to reactive foil 14 and each other making stronger and more consistent bonds.

In accordance with a preferred embodiment, the openings in the reactive foil may be implemented by designing the foil layers to crack after reacting, as shown in Fig. 5. The designed cracking may be achieved by any known method. For example, by controlling the thermal expansion mismatch in the foil 14. The foil 14 may be 20 alternatively designed to crack on reaction as it densifies. The degree of densification can be altered or controlled by varying the composition of the reactants.

In some cracking designs in accordance with a preferred embodiment, the contraction of the foil may range from 1-20 % based on densification. Cracking may also occur because the foil will contract on cooling. The heating stage causes the joining material layers (e.g., braze, solder, combination, etc.) to flow over foil 14. As the layers cool, foil 14 is restricted as to its length, so as it densifies, cracks 24 appear along foil 14 as it is pulled apart by the cooling joining material layers 12. To control the formation of cracks 24, the foil constituent materials are preferably chosen for high densification properties, high reaction temperatures, and large expansion coefficient (CTE) (i.e., the amount of foil contraction upon cooling). In a preferred embodiment, CTE is selected within a range of 1-20  $\mu\text{m}/\text{m}/^\circ\text{C}$ .

Similar to the formation of perforations 22 of Fig. 4, the designed cracking 24 of foil layer 14 allows joining material layers 12 (or bulk material 10) to extrude (as represented by arrows 26) through these cracks 24 upon melting, and to contact and bond with each other, as shown in Fig. 5 and Fig. 6. Upon completion of the foil bond with each other, the extruded materials form strong and consistent bonds among the bulk materials and the reactive foil.

Utilizing one or more embodiments of the invention, a number of different applications can now be performed more effectively and efficiently. For example, metallic glass bulk materials can now be joined, where the end product is a single structure made up solely of metallic glass, including the bond and reacted foil layer. It is also now possible to join bulk materials with very different chemical compositions, thermal properties, and other physical properties, that historically presented many difficulties in bonding. Semiconductor devices may be bonded to circuit boards or

other structures, and at the same time, multiple leads may be created that are intricately associated with that semiconductor device.

These joining applications are enhanced by the invention in that potential for heat damage, normally associated with such applications as soldering, brazing, and 5 welding, is avoided or at least minimized. For example, when ceramics are joined to metal using traditional braze/solder technologies, ceramics often crack or the joints fail because of mismatches in thermal contraction on cooling.

Moreover, utilizing embodiments of the invention, bulk materials may be freestanding prior to joining. This means that prior to the actual joining of the bulk 10 materials, the individual bulk substrates do not have to have any braze layer deposited directly upon them. Additionally, the bulk substrates do not require any pre-bonding of the reactive foil or other pre-treatment. The bulk materials involved may simply be held securely to either a freestanding braze layer or the freestanding reactive foil at the time of bonding for a strong and permanent joint to be created.

15 Embodiments of the invention allow bonding of at least one bulk (that is a metallic glass) with no braze associated with that bulk in the joining process. This is because the reactive foil may be designed to bond directly with a metallic glass. In accomplishing this joining process, the reactive foil can itself be designed to form a metallic glass upon reaction.

20 Embodiments of the invention further allow for superior bonding when the bulk materials include microchips or semiconductor devices. When bonding is directed to bulk materials such as semiconductor devices, the reactive foil may have composition

patterning properties. The embodiments allow the fabrication of alternating adjacent electrically insulating and conducting regions in the final reacted foil, thereby allowing a multitude of leads to be bonded and electrically isolated with a single reaction.

Additionally, in the bonding of semiconductor devices to a substrate such as a circuit

5 board, potential for damage to the device is a factor that must be taken into consideration. By using a freestanding reactive foil in accordance with a preferred embodiment of the invention to join such a semiconductor device to a substrate, little heat is generated that can be damaging to the device or to adjacent components. By using such freestanding foils, the semiconductor devices may be positioned for joining 10 to an electronic circuit board with greater freedom and ease. As described below, specific foil compositions, such as Ni/Al or Monel/Al, may be utilized. Foils of such composition will not only be far easier to handle than those of the past, but the combination of Ni, Cu and Al enables freestanding foils to have a higher thermal and electrical conductivity.

15 In a preferred embodiment of the invention, less energy is required to perform a joining application utilizing reactive foils in accordance with the invention. Functionally graded or alloyed layers as joining material allow for control over melting temperatures through selection of their composite materials. Functionally graded layers may be utilized, for example, because their melting temperature may be controlled. Ni-  
20 B films used as joining material allow for low temperature melting where the melting temperature begins at a relatively low temperature and elevates as B diffuses out of Ni, resulting in a final material with a relatively high melting point. By requiring less energy from the foil reaction, the overall heat applied to the total structure to be bonded can

be reduced, thereby minimizing damage to the materials to be bonded due to the foil reaction.

In accordance with a preferred embodiment of the invention, self-propagating braze (e.g., layers of Ni-Cu alloy alternating with layers of Ti-Zr alloy) may be used as joining material in conjunction with a reactive foil used in a joining application. The self-propagating braze would provide an energy source in addition to that provided by the reactive foil.

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## EXAMPLES

Preferred embodiments of the invention will be apparent from the following illustrative examples of various implementations of the invention.

5                   Reactive foils of Al and Ni are formed by cold-rolling 1-100  $\mu\text{m}$  sheets of Ni and Al which are stacked together. The sheets are cold-rolled several times until the layers are of the desired thickness.

10                  Instead of utilizing foils composed of multilayers of uniform thickness, a composite foil is used, in which nanolaminate reactive multilayers are deposited onto reactive microlaminate foils. In this configuration, certain sections of layers within the reactive foil will be of a nanoscale (nanolaminate), while other sections will be of micron-thick layers (microlaminate). The nanolaminate, as described above, will react easily and the reaction, once started, will self-propagate along the length of the foil without being quenched by heat losses to the surrounding braze layers or bulk components. Thus, the nanolaminate can be viewed as an igniter for the 15                  microlaminate. The section with microlaminate may not be able to sustain a self-propagating reaction at room temperature, but when heated by adjacent nanolaminate sections, it will sustain such a reaction.

20                  In fabricating these composite foils, sheets of Al and Ni are rolled to form the microlaminate section and then one vapor deposits a nanolaminate foil onto either side of this microlaminate structure. Fabrication may also be performed through vapor deposition of the full composite with the microlaminate layers deposited at much higher

rates without igniting the foil or causing unacceptable intermixing between the alternating layers during deposition.

A multilayer braze is formed that is similar to the reactive foils described above, which reacts to form a metallic glass. This multilayer braze gives off heat energy 5 upon a reaction of its alternating layers. Upon reaction, the braze would form an amorphous final product, similar to those in commercial use and to the foils described above. The heat generated by the reacting braze layers reduces the amount of reactive foil required for joining.

In accordance with a preferred embodiment of the invention, certain 10 compositions of foil may react to form amorphous alloys (metallic glass). Those foils may be combinations of layers of Ni-Cu and Ti-Zr, and as such will react to form metallic glass. When using such foils, certain properties may be attained. Metallic glasses have very good wetting capabilities. The braze layer may be excluded when using such a foil to join bulk metallic glass and in such a circumstance, once the foil 15 reacts and is joined with the metallic glass, a single bulk metallic glass may be produced.

While preferred embodiments of the invention have been described and illustrated, it should be apparent that many modifications to the embodiments and implementations of the invention can be made without departing from the spirit or scope of the invention. While the illustrated embodiments have been described 20 generically referring to the joining of bulk materials, it should be readily apparent that any materials (as well as the objects, things, device, or components in which they are embodied) that are to be coupled (permanently or temporarily) together through

soldering, brazing, welding or other known technique can be joined, bonded, or otherwise coupled together utilizing the invention. For example, the invention may be embodied in the joining of semiconductor devices to printed circuit boards and other similar joining applications. Materials such as metallic glasses (e.g., amorphous glass or liquid metals), metals (e.g., Cu) and alloys (e.g., stainless steel or Inconel), polymers, ceramics, composites, semiconductors, and numerous others in various combinations and components. The scope made available as a direct result of the advantages derived by joining materials utilizing the invention range from large scale bonding of SiC armor to Ti-Al-V tank bodies or the bonding of carbide coatings for tools and bits, to microscopic bonding of microchips to circuit boards on a micron scale.

The stimulus used to initiate the self-sustaining reaction in the reactive foils of the preferred embodiments may be any form of energy such as the impact from a sharp stylus, spark from an electrical source, heat from a filament, radiation from a laser, etc. Although the illustrated embodiments have been described as applied in an environment of air at room temperature, it should be readily apparent that the invention may be practiced in other environments including vacuum, Argon, etc.

It should be readily apparent that the quantitative data (e.g., reaction velocity, peak temperature, heating rate, etc.) of particular embodiments of the foils may easily be modified by varying elements of the reaction (e.g., composition materials A/B, thickness of layers, total thickness of foil, braze layer composition/thickness, etc.).

Although the embodiments specifically illustrated herein depict joining materials in the form of two sheets forming a sandwich around a reactive foil (as shown,

for example, by sheets 12 and foil 14 in Figs. 2 and 3), it should be apparent that any number of sheets (or other structures) of joining materials may be used, including a single layer wrapped around reactive foil 14. In accordance with a preferred embodiment, no layer of joining material at all may also be used. For example, metallic 5 glass bulk material, metallic glass reactive foils, or both may be used in joining applications without the use of joining material (e.g., braze).

Moreover, although the illustrated embodiments have only utilized two different materials A/B as alternating layers in a reactive foil, it should be apparent that any number of material layers can be utilized to form a reactive foil in accordance with 10 the invention.

In addition, many of the preferred embodiments disclosed herein (e.g., patterning foils, designed cracking or perforations in the foil, etc.) make particular use of freestanding foils, it should be readily apparent, however, that these embodiments and other aspects of the invention may be implemented without use of freestanding 15 foils (i.e., with foils attached to the substrates). Furthermore, it should be readily apparent that the intentionally designed openings in the reactive foil surface may penetrate through any number of layers in the foil, although it is preferred that the entire foil structure be penetrated, as shown, for example, in Fig. 6. The openings, while depicted in Fig. 4 as circle-shaped holes 22, may be any single (or combination) 20 of shapes forming one or more patterned structures on the reactive foil. The openings may be formed vertically in the direction normal to the layers of the reactive foil, or be formed at one or more angles through the layers of the foil. The openings may further be designed as a combination of perforated holes and cracks.

Accordingly, the invention is not to be seen as limited by the foregoing description, illustrations, preferred embodiment, or specific examples provided herein.

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## ABSTRACT

Reactive foils and their uses are provided as localized heat sources. The reactive foil is preferably a freestanding multilayered foil structure made up of 5 alternating layers selected from materials that will react with one another in an exothermic and self-propagating reaction. Upon reacting, this foil supplies highly localized heat energy that may be applied, for example, to joining layers, or directly to bulk materials that are to be joined. This foil heat-source allows rapid bonding to occur at room temperature in many environments (e.g., air, vacuum, Argon, water, etc.). If a 10 joining material is used, the foil reaction will supply enough heat to melt the joining materials, which upon cooling will form a strong bond, joining two or more bulk materials. If no joining material is used, the foil reaction supplies heat directly to at least two bulk materials, melting a portion of each bulk, which upon cooling, form a 15 strong bond. Additionally, the foil may be designed with openings (e.g., perforations, cracks, etc.) that allow extrusion of the joining (or bulk) material through the foil to enhance bonding.

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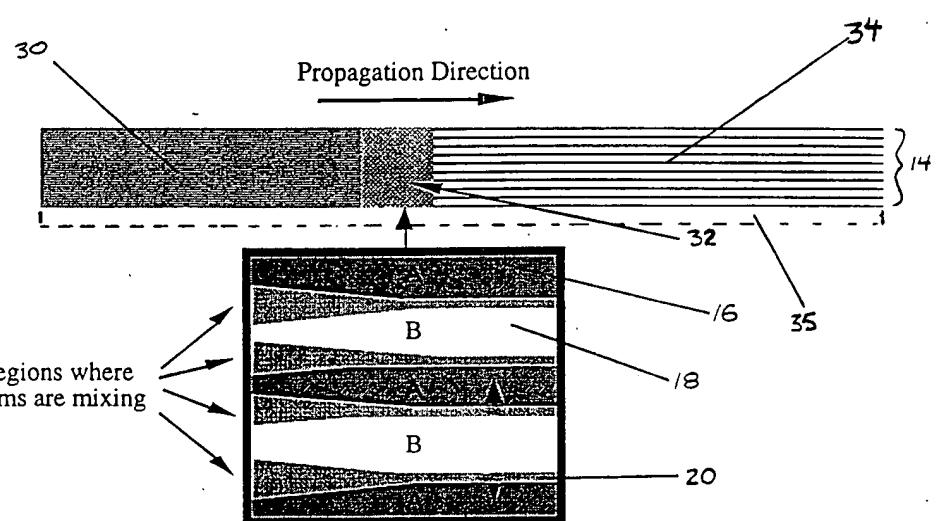


Fig. 1

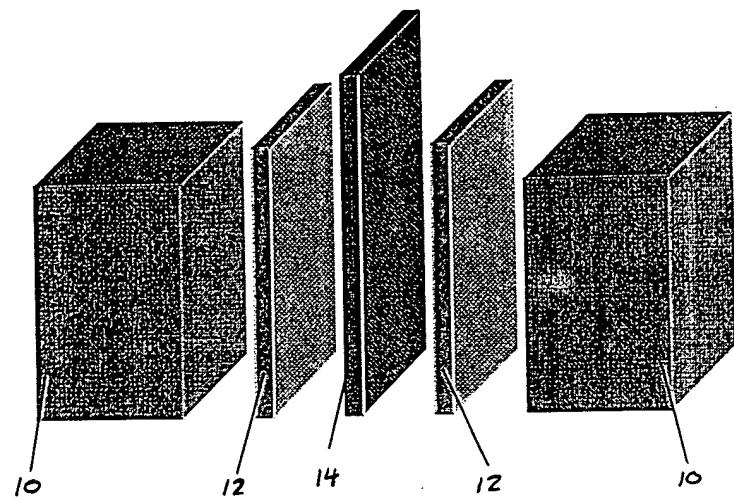


Fig. 2

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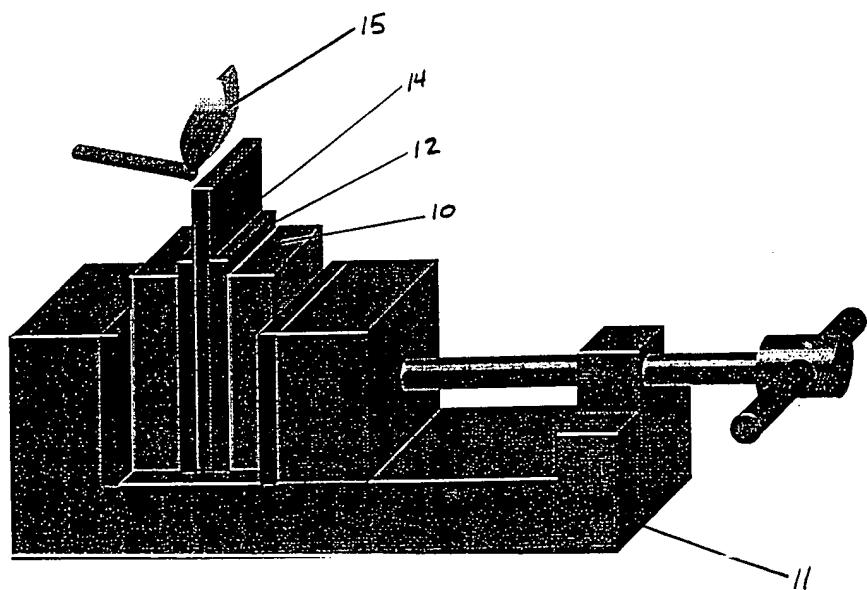


Fig. 3

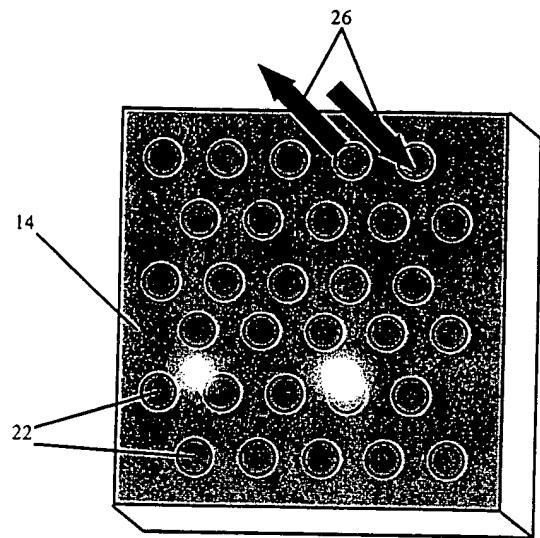


Fig. 4

FIGURE FOUR "FIGURE QUATRE"

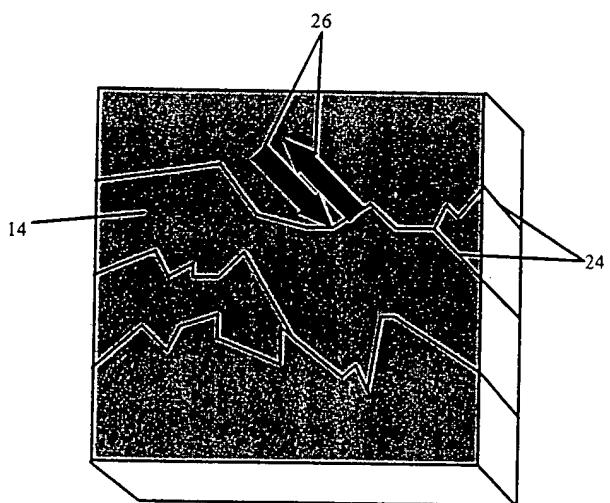


Fig. 5

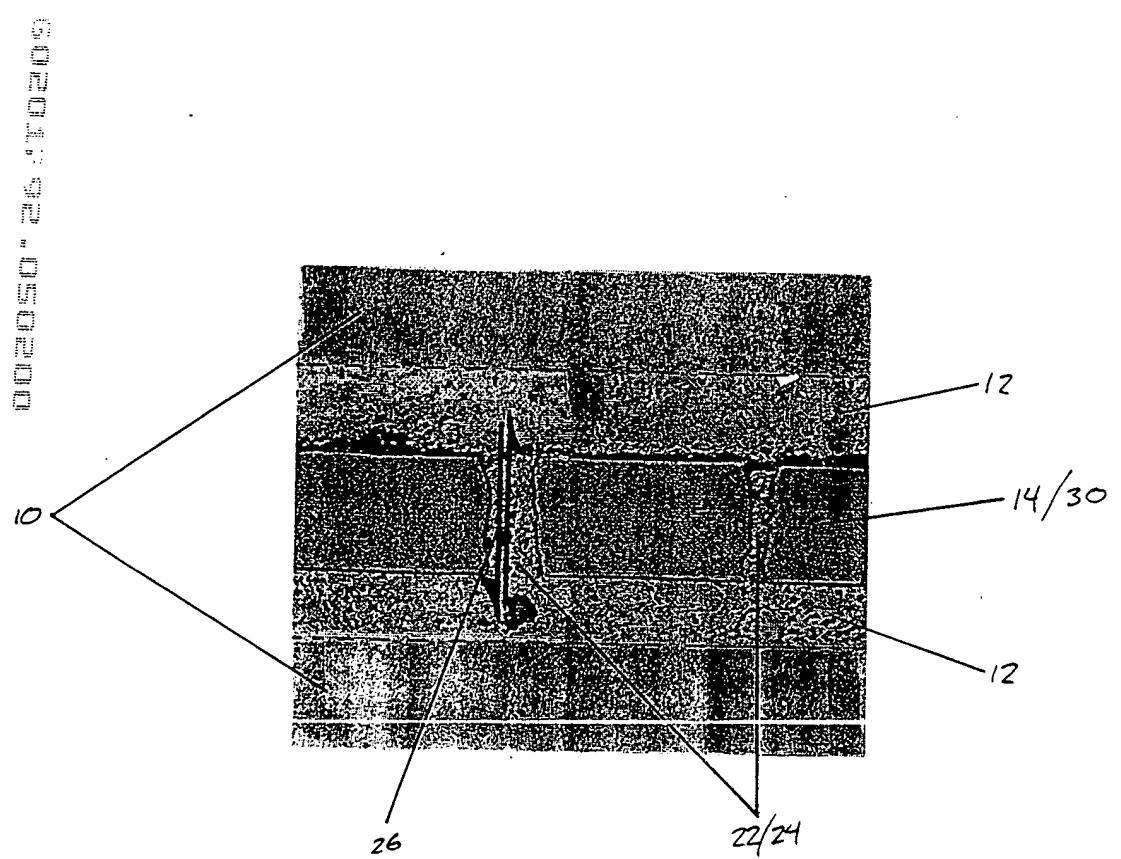


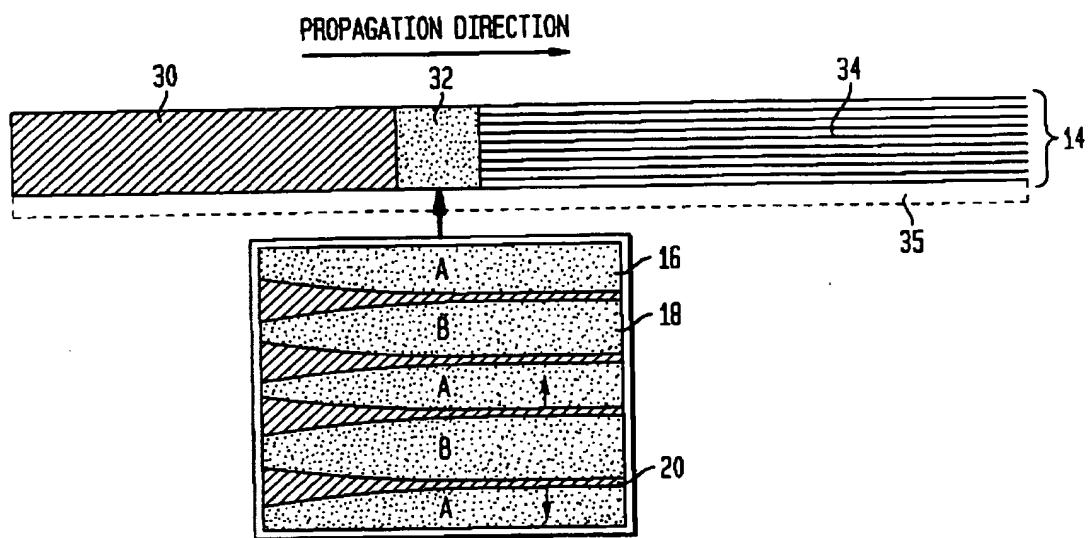
Fig. 6

Exhibit E

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FIG. 1



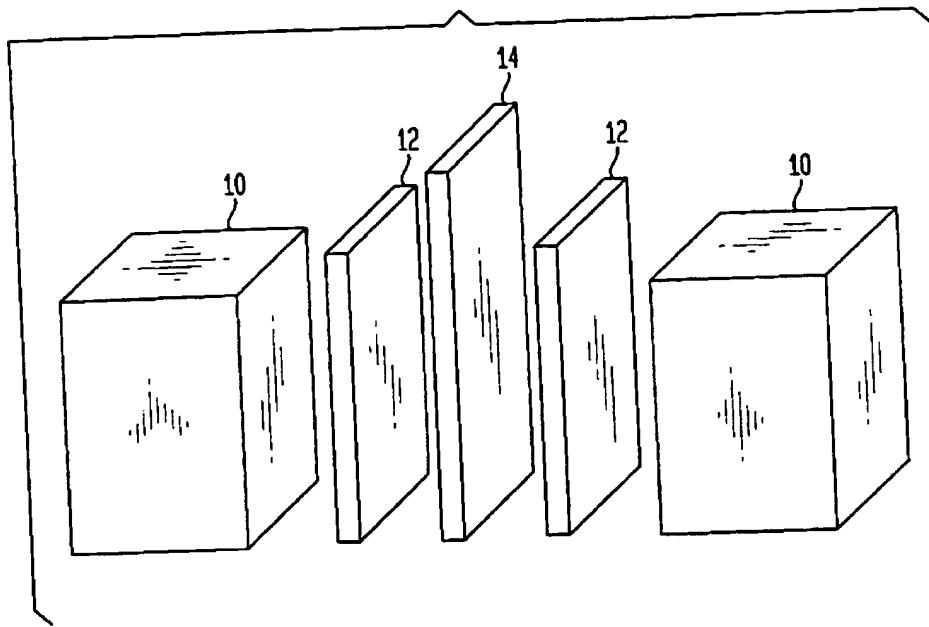
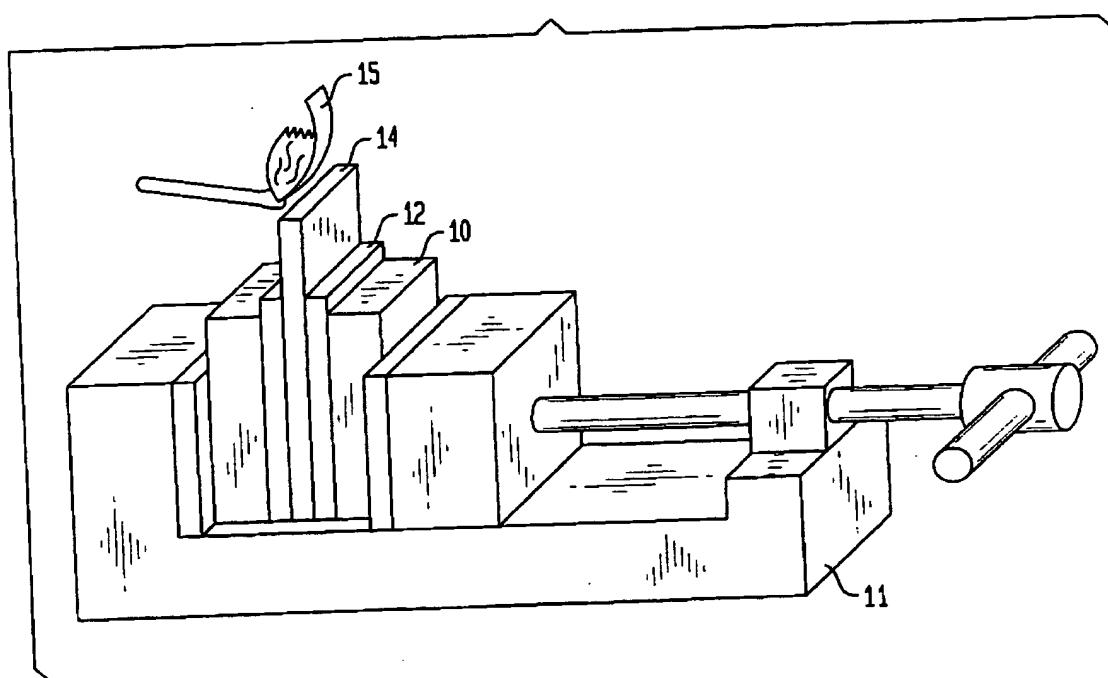
2/6  
FIG. 2

FIG. 3



316

FIG. 4

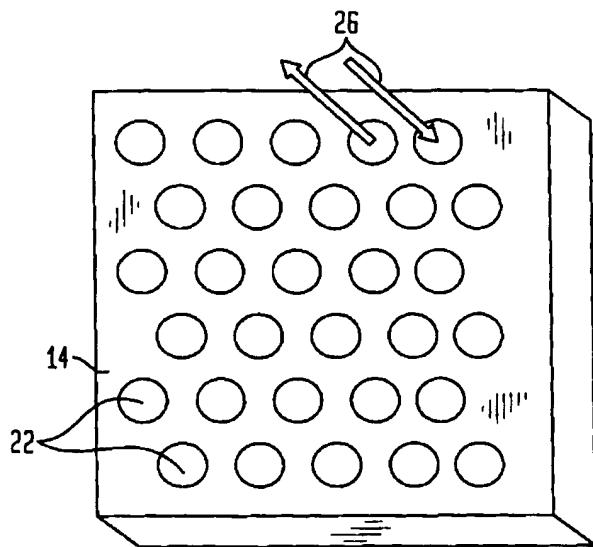
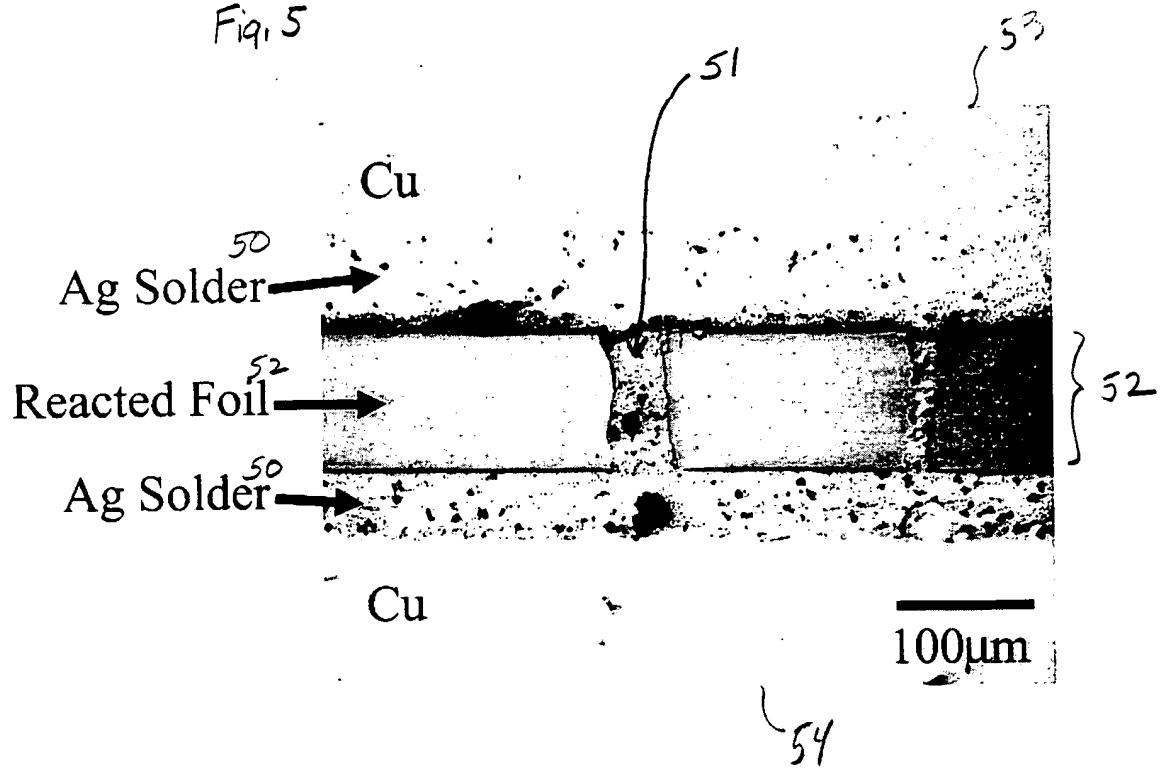


Fig. 5



4/6

Fig. 6

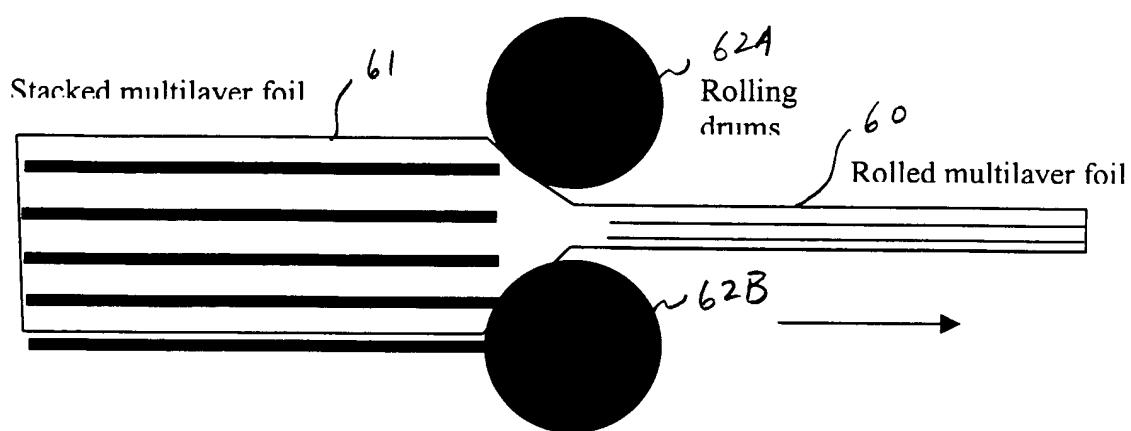
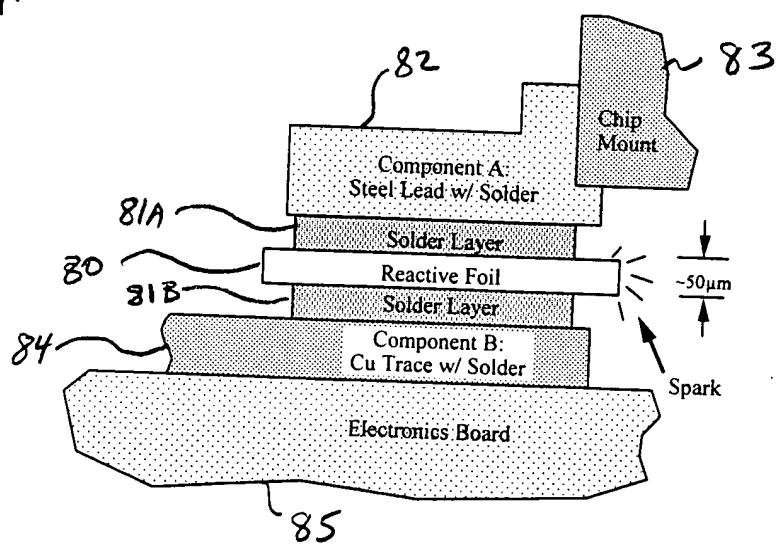
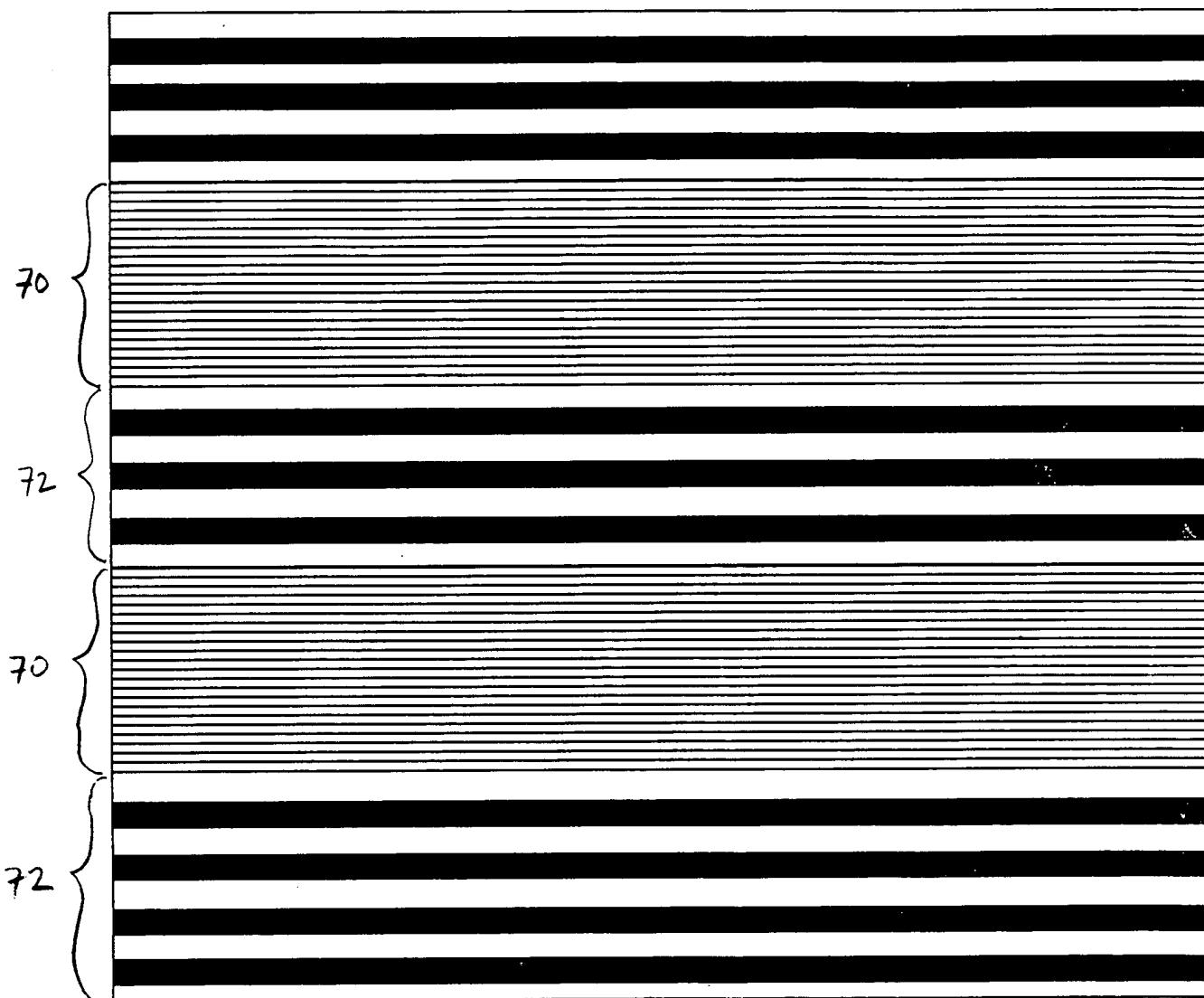


Fig. 8



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Fig. 7

 $\frac{71}{7}$ 

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Fig. 9A

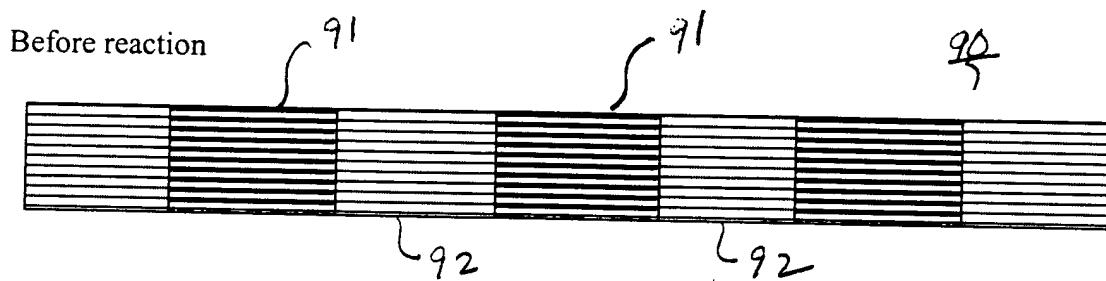


Fig. 9B

After reaction

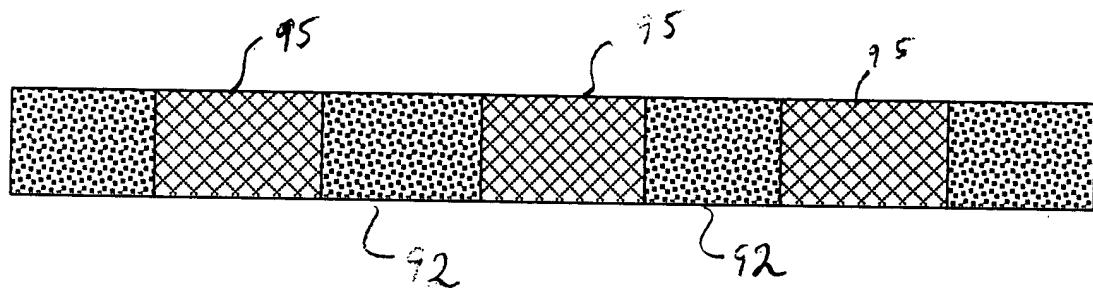


Exhibit F

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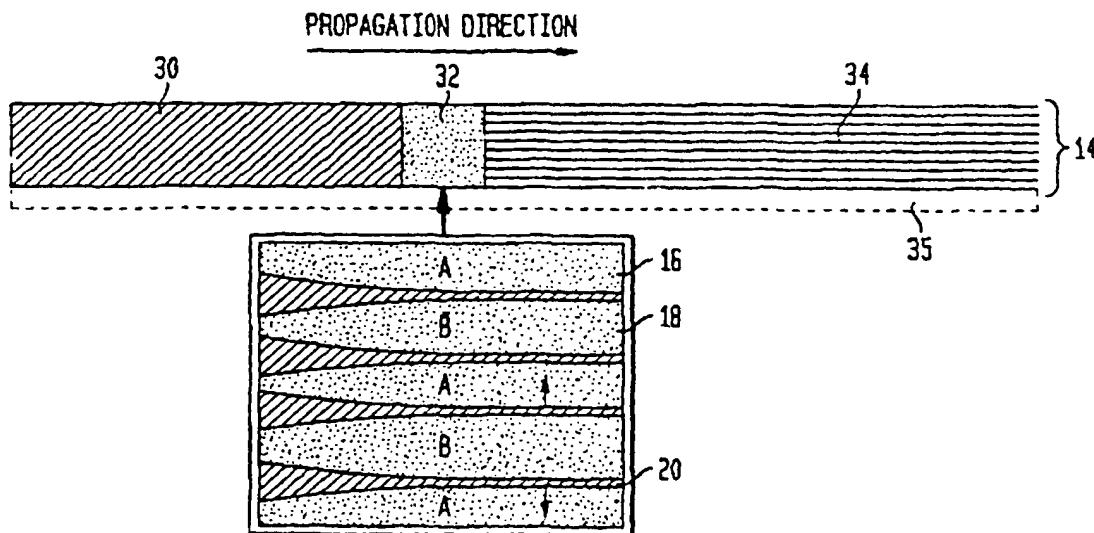
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*[Continued on next page]*

(54) Title: FREESTANDING REACTIVE MULTILAYER FOILS



WO 01/83182 A1

(57) Abstract: Reactive foils and their uses are provided as localized heat sources useful, for example, in ignition, joining and propulsion. An improved reactive foil (14) is preferably a freestanding multilayered foil structure made up of alternating layers (16, 18) selected from materials that will react with one another in an exothermic and self-propagating reaction. Upon reacting, this foil supplies highly localized heat energy that may be applied, for example, to joining layers, or directly to bulk materials that are to be joined. This foil heat-source allows rapid bonding to occur at room temperature in virtually an environment (e.g., air, vacuum, water, etc.). If a joining material is used, the foil reaction will supply enough heat to melt the joining materials. If no joining material is used, the foil reaction supplies heat directly to at least two bulk materials, melting a portion of each bulk, which upon cooling, form a strong bond. Additionally, the foil (14) may be designed with openings that allow extrusion of the joining (or bulk) material through the foil to enhance bonding.



**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**FREESTANDING REACTIVE MULTILAYER FOILS****GOVERNMENT INTEREST**

This invention was made with government support under NSF Grant  
5 Nos. DMR-9702546 and DMR-9632526 and The Army Research Lab/Advanced  
Materials Characterization Program through Award No. 019620047. The  
government has certain rights in the invention.

**CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of United States Provisional  
10 Application Serial No. 60/201,292 filed by the present applicants on May 2, 2000  
and entitled "Reactive Multilayer Foils". It is related to U.S. Application Serial No.  
\_\_\_\_\_ filed by M.E. Reiss *et al.* concurrently herewith and entitled  
"Method of Making Reactive Multilayer Foil and Resulting Product" and U.S.  
15 Application Serial No. \_\_\_\_\_ filed by T.P. Weihs *et al.* concurrently herewith  
and entitled "Reactive Multilayer Structures For Ease of Processing and Enhanced  
Ductility". These three related applications are incorporated herein by reference.

**FIELD OF THE INVENTION**

This invention relates to reactive multilayer foils, especially freestanding  
multilayer foils, useful as local heat sources.

20

**BACKGROUND OF THE INVENTION**

Reactive multilayer coatings are useful in a wide variety of applications  
requiring the generation of intense, controlled amounts of heat in a planar region.  
Such structures conventionally comprise a succession of substrate-supported

coatings that, upon appropriate excitation, undergo an exothermic chemical reaction that spreads across the area covered by the layers generating precisely controlled amounts of heat. While we will describe these reactive coatings primarily as sources of heat for welding, soldering or brazing, they can also be used in other 5 applications requiring controlled local generation of heat such as propulsion and ignition.

In many methods of bonding or joining materials, a heat source is required. This heat source may either be external or internal to the structure to be joined. When external, the heat may be generated from a device such as a furnace. 10 Processes incorporating such heat sources require the heating of the entire unit to be bonded, including the bulk materials and the bond material, to a temperature high enough to melt the bond material. Such a method presents problems because the bulk materials to be joined are often delicate or sensitive to the high temperatures required in the process. These high temperatures may damage the materials to be 15 bonded.

To alleviate the problems associated with external heat sources, internal heat sources are utilized. These heat sources often take the form of reactive powders or even electrical wires. When reactive powders are used, a mixture of metals or compounds that will react exothermically in a self-propagating reaction to 20 form a final compound or alloy is utilized. Such processes have existed since self-propagating powders were developed in the early 1960s, spawning what is known as Self-Propagating, High-Temperature Synthesis (SHS). SHS reactions, however, often require substantial preheating to self-propagate, and controlling the rate and

manner in which their energy is released is often difficult. As a result, bonding may be inconsistent or insufficient.

To combat the problems associated with reactive powder bonding, multilayer structures comprised of materials, which allow similar exothermic reactions, have been developed. Such structures allow for more controllable and consistent heat generating reactions. The basic driving force behind such SHS reactions is a reduction in atomic bond energy. When a structure having a series of layers of reactive material (known as a foil) is ignited, heat is produced as the distinct layers atomically combine. This heat ignites adjacent regions of the foil, thereby allowing the reaction to travel the entire length of the structure, generating heat until all material is reacted. Even with such advances in bonding technology, however, there remain problems. Many materials, for example, posed major difficulties and previously could not be successfully bonded. Additionally, methods utilizing reactive foils as heat sources often resulted in the foil debonding from the substrate upon reaction, thereby weakening the bond. Accordingly there is a need for improved reactive multilayer foils.

#### SUMMARY OF THE INVENTION

Reactive foils and their uses are provided as localized heat sources useful, for example, in ignition, joining and propulsion. An improved reactive foil 20 is preferably a freestanding multilayered foil structure made up of alternating layers selected from materials that will react with one another in an exothermic and self-propagating reaction. Upon reacting, this foil supplies highly localized heat energy that may be applied, for example, to joining layers, or directly to bulk materials that

are to be joined. This foil heat-source allows rapid bonding to occur at room temperature in virtually any environment (e.g., air, vacuum, water, etc.). If a joining material is used, the foil reaction will supply enough heat to melt the joining materials, which upon cooling will form a strong bond, joining two or more bulk materials. If no joining material is used, the foil reaction supplies heat directly to at least two bulk materials, melting a portion of each bulk, which upon cooling, form a strong bond. Additionally, the foil may be designed with openings that allow extrusion of the joining (or bulk) material through the foil to enhance bonding.

#### BRIEF DESCRIPTION OF THE DRAWINGS

10 Many advantages, features, and applications of the invention will be apparent from the following detailed description of preferred embodiments of the invention, which is provided in connection with the accompanying drawings. In the drawings:

Fig. 1 illustrates an exemplary multilayer reactive foil during reaction;

15 Fig. 2 shows the freestanding elements of an exemplary joining application;

Fig. 3 illustrates initiation of a joining application;

Fig. 4 shows an exemplary perforated reactive foil;

Fig. 5 depicts the flow of joining material through holes in a foil;

20 Fig. 6 illustrates formation of a reactive foil by cold rolling;

Fig. 7 is a schematic cross section of a composite reactive foil composed of sets of microlaminate foils and nanolaminate foils;

Fig. 8 shows the use of reactive foil to join a semiconductor or microelectronic device to a substrate; and

5 Figs. 9A and 9B illustrate a patterned reactive foil wherein some regions react to form conductive regions and others form non-conductive regions.

It is to be understood that these drawings are for the purpose of illustrating the concepts of the invention and are not to scale.

#### DETAILED DESCRIPTION

10 Preferred embodiments and applications of the invention will now be described. Other embodiments may be realized and compositional or structural changes may be made without departing from the spirit or scope of the invention. Although the embodiments disclosed herein have been particularly described as joining or bonding bulk materials utilizing a freestanding, self-propagating reactive foil structure, it should be readily apparent that the invention may be embodied for 15 other uses or applications requiring an intense localized heat source.

In accordance with a preferred embodiment of the invention, a multilayer reactive structure (generically referred to herein as a "foil") is provided as a local heat source in a variety of applications such as a process for joining two 20 or more (of the same or different) materials together. As illustrated in Fig. 1, reactive multilayer foil 14 is made up of alternating layers 16 and 18 of materials A and B, respectively. These alternating layers 16 and 18 may be any materials

5 amenable to mixing of neighboring atoms (or having changes in chemical bonding) in response to a stimulus, including silicides (e.g., Rh/Si, Ni/Si, and Zr/Si, etc.), aluminides (e.g., Ni/Al, Ti/Al, Monel/Al, and Zr/Al, etc.), borides (e.g. Ti/B), carbides (e.g., Ti/C), thermite reacting compounds (e.g., Al/Fe<sub>2</sub>O<sub>3</sub> or Al/Cu<sub>2</sub>O), alloys, metallic glasses, and composites (e.g., metal ceramic).

10 The materials (A/B) used in fabrication of the reactive foil are preferably chemically distinct. In a preferred embodiment, layers 16, 18 alternate between a transition metal (e.g., Ti, Ni, etc.) and a light element (e.g., B, Al, etc.). Preferably, the pairs (A/B) of elements are chosen based on the way they react to form stable compounds with large negative heats of formation and high adiabatic reaction 15 temperatures, as described in T.P. Weihs, "Self-Propagating Reactions in Multilayer Materials," Handbook of Thin Film Process Technology, 1997, which is incorporated herein by reference in its entirety. In a preferred embodiment, at least one of the layers of the reactive foil is (or contains) Al.

15 When a multilayer foil 14 is exposed to a stimulus (e.g., spark, energy pulse, etc.), for example at one end, neighboring atoms from materials A and B mix, e.g. as shown in region 30. The change in chemical bonding caused by this mixing results in a reduction in atomic bond energy, thus generating heat in an exothermic chemical reaction. This change in chemical bonding occurs as layers 20 with A-A bonds (i.e., layer 16) and layers with B-B bonds (i.e., layer 18) are exchanged for A-B bonds, thereby reducing the chemical energy stored in each layer, and generating heat. As Fig. 1 further illustrates, this generated heat diffuses through foil 14 (in a direction from reacted section 30 through reaction zone 32 to

unreacted section 34) and initiates additional mixing of the unreacted layers. As a result, a self-sustaining/self propagating reaction (SHS reaction) is produced through foil 14. With sufficiently large and rapid heat generation, the reaction propagates across the entire foil 14 at velocities typically greater than 1 m/s. As the 5 reaction does not require additional atoms from the surrounding environment (as, for example, oxygen in the case of combustion), the reaction makes foil 14 a self-contained source of energy capable of emitting bursts of heat and light rapidly, reaching temperatures above 1400 K, and a local heating rate reaching  $10^9$  K/s. This energy is particularly useful in applications (e.g., joining, ignition, etc.) 10 requiring production of heat rapidly and locally.

When a reaction propagates across a multilayer foil 14 as illustrated by Fig. 1, the maximum temperature of the reaction is typically located at the trailing edge of the reaction zone 32. This may be considered the final temperature of reaction, which can be determined by the heat of reaction ( $\Delta H_{rx}$ ), the heat lost to the 15 environment or surrounding material ( $\Delta H_{env}$ ), the average heat capacity of the sample ( $C_p$ ), and the mass of the sample, M. Another factor in determining the final temperature is whether or not the reaction temperature exceeds the melting point of the final product. If the melting point is exceeded, then some heat is absorbed in the state transformation from solid to liquid of the product. The final temperature 20 of reaction may be determined using the following formulas (where  $T_0$  is the initial temperature,  $\Delta H_m$  is the enthalpy of melting,  $T_m$  is the melting temperature of the product, and there is no reaction with the surrounding environment or material), depending upon whether final product melting occurs:

$$T_f = T_0 - (\Delta H_{rx} + \Delta H_{env}) / (C_p M) \quad \text{If no melting of final product}$$

occurs;

$T_f = T_m$       If there is a two-phase region of solid and liquid final product;  
and

5       $T_f = T_0 - (\Delta H_{rx} + \Delta H_{env} + \Delta H_m) / (C_p M)$     If the final product completely  
melts.

Intricately related to the heat of the foil reaction is the velocity of the propagation of the reaction along the length of foil 14. The speed at which the reaction can propagate depends on how rapidly the atoms diffuse normal to their 10 layering (Fig. 1) and how rapidly heat is conducted along the length of foil 14. The propagation velocity is a strong function of the thicknesses of the individual layers in the multilayer foil. As the thickness of individual layers 16, 18 decreases, the diffusion distances are smaller and atoms can mix more rapidly. Heat is released at a higher rate, and therefore the reaction travels faster through the foil structure.

15      In accordance with a preferred embodiment of the invention, reactive multilayer foils 14 may be fabricated by physical vapor deposition (PVD) methods. A magnetron sputtering technique, for example, may be used to deposit the materials A/B on a substrate (shown in Fig. 1 in dashed outline form as layer 35) as alternating layers 16, 18. Substrate 35 may be rotated over two sputter guns in a 20 manner well known in the art to effectuate the layering of materials A/B into alternating layers 16, 18.

Substrate 35 is shown in dashed outline form to indicate that it is a removable layer that facilitates fabrication of the reactive foil 14 as a freestanding foil. Substrate 35 may be any substrate (e.g., Si, glass, or other underlayer) having the characteristics of providing sufficient adhesion so as to keep the foil layers on the substrate during deposition, but not too adhesive to prevent the foil from being removed from the substrate following deposition. The substrate can include a coating of release material or adhesion material to fine tune its adhesion characteristics.

Advantageously an additional wetting layer (e.g., tin) may be used as an interface layer between the first layer of foil (16 or 18) and the substrate 35 to provide the necessary adhesive. When no wetting layer is employed, selection of the appropriate material A/B as the first layer deposited on the substrate will ensure that the necessary adhesive requirements are met. When a reactive foil using Al/Monel as materials A/B is to be fabricated, for example, without a wetting layer, the exemplary reactive foil would be deposited on a substrate such as Si with the first layer being Al deposited on the substrate. Al is preferably selected as the first layer in such case because Al will sufficiently adhere to Si during depositing, but will allow peeling off of the substrate after the foil is formed.

A fabricated foil 14 may have hundreds to thousands of alternating layers 16 and 18 stacked on one another. Individual layers 16 and 18 preferably have a thickness ranging from 1-1000 nm. In a preferred embodiment, the total thickness of foil 14 may range from 10 $\mu$ m to 1cm.

Another method of fabricating is to deposit material in a codeposition geometry. Using this method, both material sources are directed onto one substrate and the atomic fluxes from each material source are shuttered to deposit the alternate layers 16 and 18. An alternative method is to eliminate shuttering 5 altogether and rotate substrates over two material sources that have physically distinct atomic fluxes. With this method, each pass over a source preferably generates an individual layer.

Preferably the degree of atomic intermixing of materials A/B that may occur during deposition should be minimized. This may be accomplished by 10 depositing the multilayers onto cooled substrates, particularly when multilayers 16 and 18 are sputter deposited. To the extent that some degree of intermixing is unavoidable, a relatively thin (as compared to the alternating unreacted layers) region of pre-reacted material 20 will be formed. Such a pre-reacted region 20, nevertheless, is helpful in that it serves to prevent further and spontaneous reaction 15 in foil 14.

In an alternative embodiment, a multilayer reactive foil may be fabricated using mechanical techniques such as repeated rolling of layered composites.

As illustrated in Fig. 1, the preferred reactive foil 14 is a freestanding 20 multilayer reactive foil for particular use as a heat-generating source. Freestanding foils are easier to characterize than thin films because they can be handled like "bulk" samples. Making reactive foils 14 freestanding greatly expands their possible uses. Because such reactive foils are not necessarily associated with any

particular application, they may be mass-produced for any purpose requiring a self-propagating localized heat source. Their production is not limited or impeded by placing large or delicate items into a vacuum chamber to be coated by a reactive multilayer foil. Moreover, freestanding foils will allow heat sinking to the substrate 5 to be minimized where unwanted.

Freestanding foils in accordance with preferred embodiments of the invention may be adapted for use in a variety of applications. For example, the freestanding foils may be used to couple bodies of materials (referred to herein as "bulk materials") together to form a unified product. Freestanding foils may find 10 use in any number of bonding, soldering, brazing, welding or other applications to join bulk materials. A typical joining application is represented in Fig. 3, in which two or more bulk materials 10 are to be joined together. The bulk materials 10 may be ceramics, metallic glasses, metals/alloys, polymers, composites, semiconductors, and other forms of material.

15 In the particular joining application illustrated in Fig. 3, joining material 12 is used to join bulk materials 10 together. Joining material 12 may be any layer (or composite layer) of material to be melted to join bulk materials 10 together. Joining material 12 can be in the form of freestanding sheets made up of metallic glasses, metals/alloys, functionally graded layers, Ni-B films, solder, brazes, self-propagating braze, combinations of such, or other like joining materials.

20 In accordance with a preferred embodiment of the invention, a reactive foil 14 is positioned between joining materials 12 to form a structure somewhat like a sandwich. The reactive foil "sandwich" thus formed is preferably positioned

between bulk materials 10 at the location (e.g., end point, joint, intersection, etc.) at which the bulk materials 10 are to be joined together.

Alternatively, a reactive foil 14 is positioned between bulk materials 10 which have previously been coated with joining materials 12.

5 As another alternative, a reactive foil 14 is positioned between joining materials 12 to form a structure somewhat like a sandwich. The reactive foil "sandwich" thus formed is preferably positioned between bulk materials 10 at the location (e.g., end point, joint, intersection, etc.) at which the bulk materials 10 are to be joined together. The bulk materials are first coated with joining materials.

10 The joining process involves the application of force (as symbolically represented by vice 11 in Fig. 3) to maintain the relative positions of bulk materials 10, joining materials 12, and reactive foil 14. Advantageously all components are freestanding elements pressed together. In an alternative embodiment, joining materials 12 are pressed as a composite with reactive foil 14.

15 Once the components of the joining process are positioned, a stimulus (shown as lighted match 15) is applied, preferably, to one end of reactive foil 14 to initiate an SHS reaction. The intermixing of atoms within reactive foil 14 produces rapid and intense heat sufficient to melt joining materials 12 along the entire length of reactive foil 14. In this state, joining materials 12 are sufficient to join bulk materials 10 together. Shortly thereafter, the joined materials 10 return to the temperature of the environment (e.g., room temperature) and can be removed from the applied force (graphically represented by vice 11).

A composite structure composed of joining materials 12 and reactive foil 14 can be formed through deposition (e.g., vapor depositing) of reactive foil 14 onto one layer of joining material 12. Another layer of joining material is then combined with reactive foil 14 through vapor deposition or an application of force (e.g., cold 5 rolling).

Advantageously a wetting/adhesion layer may be added to facilitate surface wetting for the reactive foil 14, bulk materials 10, or both. The wetting/adhesion layer allows uniform spreading of joining material to ensure consistent joining of bulk materials. The wetting/adhesion layer may be a thin layer 10 of joining material (e.g., braze), Ti, Sn, metallic glass, etc. Commercial alloys such as Ag-Sn, Ag-Cu-Ti, Cu-Ti, Au-Sn, and Ni-B may also be used.

Preferred embodiments of the invention are useable as freestanding reactive foils 14 with increased total thickness. The total thickness of such a reactive foil depends upon the thickness and number of the elemental layers (e.g., 15 16 and 18) utilized to form the foils. Foils that are less than 10  $\mu\text{m}$  are very hard to handle as they tend to curl up on themselves. Foils on the order of 100  $\mu\text{m}$  are stiff, and thus, easily handled. Thicker foils also minimize the risk of a self-propagating reaction being quenched in the foils. In joining applications using reactive foils, 20 there is a critical balance between the rate at which the foil generates heat and the rate at which that heat is conducted into the surrounding braze layers and the joint to be formed. If heat is conducted away faster than it is generated, the reaction will be quenched and the joint cannot be formed. The thicker foils make it harder to

quench the reaction because there is a larger volume generating heat and the same surface area through which heat is lost.

Thicker foils can be utilized with reaction temperatures that are lower, generally leading to more stable foils. Foils with high formation reaction 5 temperatures are generally unstable and brittle and therefore are dangerous and difficult to use. Brittle foils, for example, will crack easily, leading to local hot spots (through the release of elastic strain energy and friction) that ignite the foil. Cutting such brittle foils (e.g., for specific joint sizes) is very difficult to do as they are more likely to crack into unusable pieces or igniting during the cutting process.

10 Freestanding thick foils offer the advantage of overcoming problems associated with thermal shock and densification problems that have presented obstacles in known processes. Both phenomena relate to rapid changes in the dimensions of the foils. On reacting, the foils will heat rapidly and will try to expand beyond the substrate that constrains them. This leads to a thermal shock and foils that are 15 deposited on substrates can debond, thereby causing inconsistent and less effective bonding. As the reaction proceeds, the foils will also densify, due to the change in chemical bond. This densification, can also cause debonding from a substrate and inconsistent and ineffective bonding. By making the foil freestanding in accordance with a preferred embodiment of the invention, no debonding occurs, the 20 foil is easily manipulated and handled, and thus the reactive foil is made available to a greater variety of applications.

In accordance with a preferred embodiment, the thicker reactive foils are on the order of 50 $\mu$ m to 1cm thick. Although a number of different systems may be

employed to create the thick freestanding reactive foils, a unique process in selecting the fabrication conditions for the employed system should be carefully selected. For example, deposition conditions such as sputter gas and substrate temperature are advantageously chosen so that stresses remain sufficiently low in the films of the foil as they are grown in the system. Since the stress in the film times its thickness scales with the driving force for delamination, the product of stress and thickness should be kept below 1000 N/m. Stresses often arise in the films during the fabrication process. As the films grow thicker, they are more likely to peel off their substrates or crack their substrates than thinner films, thereby ruining the final foil production. By characterizing the stresses in the films and selecting conditions to minimize the stresses, the fabrication process can be completed without the premature peeling off of the foil or the cracking of the substrate.

In an alternative embodiment, openings in a reactive foil are intentionally designed in the foil structure. These openings are of particular use in facilitating and enhancing joining applications.

The foil may be initially fabricated, for example, with one or more openings or perforations 22 through the foil structure, as shown in Fig. 4. Preferably the openings are formed in a periodic pattern, such as a rectangular array, across the foil area. Any known method may be employed to create openings. For example, sputter depositing of the foil 14 on a removable substrate with patterned holes may be used. The openings may also be formed by depositing the foil 14 onto a substrate, depositing photoresist on the foil, patterning the

photoresist with photolithography, and then etching the underlying foil through the patterned holes. A further exemplary technique involves physically punching holes in foil 14. Preferably the openings have effective diameters in the range of 10 - 10,000 micrometers. (The effective diameter of a non-circular opening is the 5 diameter of a circular opening of equal area.)

As shown in Fig. 4, the openings in foil 14 allow joining material 12, or bulk material 10 in some circumstances, to extrude (as shown by arrows 26) through these perforations 22 upon being heated and melted by the exothermic reaction of foil 14. Upon this extrusion, one layer of joining material 12, or bulk 10 material 10, may contact and couple with another layer 12, or bulk material 10, on the opposite side of the freestanding foil 14. The patterned perforations 22 permit enhanced bonding of bulk materials 10 to reactive foil 14 and each other making stronger and more consistent bonds.

Fig. 5 is a microphotograph showing two copper bodies 53, 54 bonded 15 by silver solder 50 that has extruded through openings, e.g. 51 in a reacted foil 52.

Utilizing one or more embodiments of the invention, a number of different applications can now be performed more effectively and efficiently. For example, metallic glass bulk materials can now be joined, where the end product is a single structure made up solely of metallic glass, including the bond and reacted 20 foil layer. It is also now possible to join bulk materials with very different chemical compositions, thermal properties, and other physical properties, that historically presented many difficulties in bonding. Semiconductor or microelectronic devices may be bonded to circuit boards or other structures, and at the same time, multiple

leads may be created that are intricately associated with the devices.

Semiconductor and microelectronic devices may also be sealed hermetically.

These joining applications are enhanced by the invention in that potential for heat damage, normally associated with such applications as soldering, 5 brazing, and welding, is avoided or at least minimized.

Moreover, utilizing embodiments of the invention, the bulk materials being joined may be freestanding. This means that prior to the actual joining of the bulk materials, the individual bulk substrates do not need any braze layer deposited directly upon them. Additionally, the bulk substrates do not necessarily require any 10 pre-bonding of the reactive foil or other pre-treatment. The bulk materials involved may simply be held securely to either a freestanding braze layer or the freestanding reactive foil at the time of bonding for a strong and permanent joint to be created.

Embodiments of the invention allow bonding at least one bulk that is a metallic glass. No braze need be associated with that bulk in the joining process. 15 This is because the reactive foil may be designed to bond directly with a metallic glass upon reaction. To accomplish this joining process, the reactive foil can itself react to form a metallic glass.

Embodiments of the invention further allow for superior bonding when the bulk materials include microchips or semiconductor devices. In the bonding of 20 semiconductor devices to a substrate such as a circuit board, potential for damage to the device is a factor that must be taken into consideration. By using a freestanding reactive foil to join such a semiconductor device to a substrate, little heat is

generated that can be damaging to the device or to adjacent components. The semiconductor devices may be situated on the substrate with greater freedom and ease. As described below, specific foil compositions, such as Ni/Al or Monel/Al, may be utilized. Foils of such composition are not only far easier to handle than those of the past, but the combination of Ni, Cu and Al enables freestanding foils to have a high thermal and electrical conductivity.

When bonding is directed to bulk materials such as semiconductor devices, the reactive foil may have composition patterning properties. The embodiments allow the fabrication of alternating adjacent electrically insulating and 10 conducting regions in the final reacted foil, thereby allowing a multitude of leads to be bonded and electrically isolated with a single reaction.

In a preferred embodiment of the invention, less energy is required to perform a joining application utilizing reactive foils. Functionally graded layers as joining material allow for control over melting temperatures through selection of 15 their composite materials. Functionally graded layers may be utilized, for example, because their melting temperature may be controlled. Ni-B films used as joining material allow for low temperature melting where the melting temperature begins at a relatively low temperature and elevates as B diffuses out of Ni, resulting in a final material with a relatively high melting point. By requiring less energy from the foil reaction, the overall heat applied to the total structure to be bonded can be reduced, 20 thereby minimizing damage to the materials to be bonded due to the foil reaction.

In another embodiment, one may include layers of reactive multilayer braze within the reactive multilayer foil. For example, in a foil comprising reactive

layers of Al and reactive layers of Ti, Zr or Hf alloys, one may include one or more reactive braze layers comprising a Cu or a Ni alloy. The reactive multilayer braze would provide an energy source as the layers mix and form the joining material, in addition to the energy provided by the reactive foil. The combination of reactive 5 multilayer foil and reactive multilayer braze permits the use of reactive braze that may not self-propagate without the foil.

## EXAMPLES

The invention may now be more clearly understood by consideration of the following specific examples:

### 5 Example 1

Reactive foils of Al and Ni are formed by cold rolling many 5  $\mu\text{m}$  sheets of Ni and Al that are stacked together. Fig. 6 schematically illustrates fabrication of the foil 60 by passage of the stack 61 between rollers 62A and 62B. The sheets can be cold-rolled several times until the layers are reduced to the 10 desired thickness.

### Example 2

Instead of utilizing foils comprised of multilayers of uniform thickness, a composite foil is used, in which nanolaminate reactive multilayers are deposited onto reactive microlaminate foils. As illustrated in Fig. 7 certain sections of layers 15 70 within the reactive foil 71 will be of a nanoscale (nanolaminate), while other sections 72 will be of micron-thick layers (microlaminate). The nanolaminate, as described above, will react easily and the reaction, once started, will self-propagate along the length of the foil without being quenched by the melting of the surrounding braze layers or bulk components. Thus, the nanolaminate can be 20 viewed as an igniter for the microlaminate. The section 72 with microscale layers may not be able to sustain a self-propagating reaction at room temperature, but when heated by adjacent nanolaminate sections 70, it will sustain such a reaction. The foil can comprise alternate layers of Al and Ni.

**Example 3**

In fabricating these composite foils, sheets of Al and Ni are rolled to form the microlaminate section and then a nanolaminate foil is vapor deposited onto either side of this microlaminate structure. Fabrication may also be performed 5 through vapor deposition of the full composite with the microlaminate layers deposited at much higher rates without igniting the foil or causing unacceptable intermixing between the alternating layers during deposition.

**Example 4**

A reactive multilayer braze is formed that is similar to the reactive foils 10 described above, which reacts to form a metallic glass. This multilayer braze gives off heat upon a reaction of its alternating layers. Through a careful selection of reactants that are known to be good glass formers, the braze will form an amorphous final product upon reaction, similar to those in commercial use and to the foils described above. The heat generated by the reacting braze layers reduces the 15 amount of reactive foil required for joining.

**Example 5**

Certain compositions of foil 14 may react to form amorphous alloys 20 (metallic glass). Those foils may be combinations of layers of alloys that comprise Ni or Cu, alloys that comprise Ti, Zr, or Hf, and alloys that comprise Al as such will react to form metallic glass. When using such foils, certain properties may be attained. Metallic glasses have very good wetting capabilities. The braze layer may be excluded when using such a foil to join bulk metallic glass and in such a

circumstance, once the foil reacts and is joined with the metallic glass, a single bulk metallic glass may be produced.

#### Example 6

5 A semiconductor or microelectronic device is joined to a substrate such as a printed circuit board using a reactive multi-layer foil. Fig. 8 schematically illustrates the joining arrangement wherein the reactive foil 80 is sandwiched between solder layers 81A and 81B, and the sandwich is disposed between the contact lead 82 for the device 83 and the contact surface 84 of the board.

#### Example 7

10 A patterned reactive foil is designed so that some sections react to form electrically conductive regions and other sections form non-conductive regions.

15 Figs. 9A and 9B schematically illustrate the concept. Fig. 9A shows the foil 90 before reaction. Fig. 9 B is after the reaction. Regions 91, comprising alternate layers of Al and Ni, react to form conductive regions 95. Regions 92, comprise insulators, such as  $\text{SiO}_2$  or silicon nitride, or alternate layers that react to form non-conductive regions.

It is contemplated that in use, regions 91 would be registered between contacts above and below the foil 90 to be electrically connected through the regions 95 after the reaction.

20 It can now be seen that one aspect of the invention is a method of making a reactive multilayer foil composed of a plurality of alternating layers that

can react exothermically. The method comprises the steps of providing a substrate, vapor depositing the alternating layers on the substrate to form the multilayer foil, and separating the multilayer foil from the substrate. Advantageously the substrate has sufficient adherence to the deposited layers to retain the layers during deposition but insufficient adherence to prevent removal of the multilayer foil after deposition. As an example, the layers can comprise one or more layers of aluminum deposited in contact with a silicon substrate. Alternatively, the substrate can include a coating of release material or an adhesion material to achieve the proper level of adherence.

10 One approach for separating the multilayer foil from the substrate is to provide a substrate with a sacrificial layer (or make the entire substrate a sacrificial layer) that can be etched or peeled away from the foil after deposition. Exemplary materials for a sacrificial layer include copper, brass and photoresist.

15 The vapor depositing of the layers is preferably by physical vapor deposition such as by magnetron sputtering or electron beam evaporation. Advantageously the substrate is cooled during the vapor depositing to reduce intermixing of the alternating layers, to reduce energy losses and to reduce stresses in the deposited layers. Advantageously the layers are deposited to form a multilayer foil having a thickness in the range 50  $\mu\text{m}$  - 1 cm. Foils thus made with 20 a thickness in the range 10 $\mu\text{m}$  to 1cm can be used as freestanding foils.

Another aspect of the invention is a method of bonding a first body to a second body comprising the steps of providing a freestanding reactive multilayer foil, pressing the bodies together against the foil and igniting the reactive foil. The

ignited foil can melt material of the bodies or melt an associated meltable (joining material) layer to join the bodies together. Alternatively, the reaction product of the layers can itself be the joining material. One or both of the bodies can be semiconductor or microelectronic devices. The method is particularly 5 advantageous for joining bodies having coefficients of thermal expansion, which differ by 1  $\mu\text{m}/\text{m}^{\circ}\text{C}$  or more.

In an alternative embodiment, a reactive multilayer foil includes a plurality of openings through the thickness of the foil. The openings are preferably periodic over the foil area. These openings can be left unfilled or they can be filled 10 with meltable materials, propellants, or other materials that will change or react on heating when the reactive foil is ignited.

Such apertured foils can be made by providing a substrate having a surface including a plurality of preformed openings, bumps or particles of thickness (or depth) comparable to or larger than the thickness of the multilayer foil to be 15 deposited, depositing the reactive multilayer foil, and separating the resulting apertured multilayer foil from the substrate.

Alternatively, a reactive multilayer foil can be deposited on a substrate, patterned by a removable masking layer, and etched to form a plurality of holes. The apertured foil can then be removed from the substrate. Yet further in the 20 alternative, a continuous foil can be formed and holes can be formed in the continuous foil by mechanical pressing.

The apertured foils have an important application in bonding. A reactive foil perforated by a plurality of openings is disposed between a first and a second body. If the body material is not meltable by the foil, a separate meltable layer or coating of meltable joining material is also disposed between the bodies. The 5 bodies are pressed together against the foil (and joining material) and the foil is ignited to melt joining material. The melted material flows within and through the openings in the foil to join the bodies. This approach produces a characteristic joint with ductility enhancing bridges through the openings. It is especially advantageous where one or both bodies are semiconductor or microelectronic 10 devices or where the devices have CTEs that differ by more than  $1\mu\text{m}/\text{m}^{\circ}\text{C}$ .

A third type of novel reactive foil is a composite reactive multilayer foil in which the individual layers in the foil differ in thickness or in composition, on moving across the total thickness of the foil, to achieve advantageous results. One exemplary composite reactive multilayer foil comprises a first section with a 15 plurality of relatively thick reactive layers, e.g.  $1\mu\text{m}$  to  $10\mu\text{m}$ , stacked on a second section with a plurality of thinner reactive layers(e.g. 1-1000 nm). The section with the thinner reactive layers ignites more rapidly than would the section with the thicker reactive layers. But as ignition spreads across the thinner section, it ignites the thicker section to produce a more uniform ignition and higher heat. Similar 20 results can be achieved by variation of the foil composition in the thickness direction. Compositional variations can provide one set of layers whose reaction product provides joining material and another set of more reactive layers for igniting the first set. Compositional variations can be achieved, for example, by

varying the process parameters in vapor depositing in accordance with techniques well known in the art.

A fourth type of novel reactive foil has a major surface area composed of at least two different regions: one or more first regions which will react to form 5 electrically conductive material and one or more second regions which are non-conductive. Such foils are particularly useful in connecting semiconductor device electrical contacts to a substrate having receiving contacts. A foil can be disposed between the device and the substrate with the device contacts, the contacts of the substrate and the first regions of the foil all in registration. The device and substrate 10 are then pressed against the foil, and the foil is ignited to bond the device to the substrate with the respective contacts conductively connected and the other regions non-conductively bonded.

While preferred embodiments of the invention have been described and illustrated, it should be apparent that many modifications to the embodiments and 15 implementations of the invention can be made without departing from the spirit or scope of the invention. While the illustrated embodiments have been described generically referring to the joining of bulk materials, it should be readily apparent that any materials that are to be coupled (permanently or temporarily) together through soldering, brazing, welding or other known technique can be coupled 20 together utilizing the invention. Materials such as metallic glasses (e.g., amorphous glass), metals (e.g., Cu) and alloys (e.g., stainless steel), polymers, ceramics (e.g. SiC), composites, semiconductors, and numerous others in various combinations. The scope made available as a direct result of the advantages derived by joining

materials utilizing the invention range from large scale bonding of SiC armor to Ti-Al-V tank bodies, or the bonding of carbide coatings to tool bits, to microscopic bonding of microchips to circuit boards on a nano or microscale.

The stimulus used to initiate the self-sustaining reaction in the reactive foils of the preferred embodiments may be any form of energy such as the impact from a sharp stylus, spark from an electrical source, heat from a filament, radiation from a laser, etc. Although the illustrated embodiments have been described as applied in an environment of air at room temperature, it should be readily apparent that the invention may be practiced in other environments including vacuum, argon, 10 water, etc.

It should be readily apparent that the quantitative data (e.g., reaction velocity, peak temperature, heating rate, etc.) of particular embodiments may easily be modified by varying elements of the reaction (e.g., varying composition of materials A or B, thickness of layers, total thickness of foil, or braze layer 15 composition/thickness).

Although the embodiments specifically illustrated herein depict joining materials in the form of two sheets forming a sandwich around a reactive foil (as shown, for example, by sheets 12 and foil 14 in Figs. 2 and 3), it should be apparent that any number of sheets (or other structures) of joining materials may be used, 20 including a single layer wrapped around reactive foil 14 or joining materials attached to the bulk components. In accordance with a preferred embodiment, no layer of joining material at all may also be used. For example, metallic glass bulk

material, metallic glass reactive foils, or both may be used in joining applications without the use of joining material (e.g., braze).

Moreover, although the illustrated embodiments have only utilized two different materials A/B as alternating layers in a reactive foil, it should be apparent 5 that any number of material layers can be utilized to form a reactive foil in accordance with the invention.

In addition, many of the preferred embodiments disclosed herein (e.g., patterning foils, perforations in the foil, etc.) make particular use of freestanding foils, it should be readily apparent, however, that these embodiments and other 10 aspects of the invention may be implemented without use of freestanding foils. Furthermore, it should be readily apparent that the intentionally designed openings in the reactive foil surface may penetrate through any number of layers in the foil, although it is preferred that the entire foil structure be penetrated as shown, for example, in Fig. 5. The openings, while depicted in Fig. 4 as circle-shaped holes 15 22, may be any single (or combination) of shapes forming one or more patterned structures on the reactive foil. The openings may be formed vertically in the direction normal to the layers of the reactive foil, or be formed at one or more angles through the layers of the foil.

Thus numerous and varied other arrangements can be made by those 20 skilled in the art without departing from the spirit and scope of the invention.

What is claimed:

1. A method of making a freestanding reactive multilayer foil composed  
5 of a plurality of alternating layers that can react exothermically, comprising the  
steps of:

providing a substrate;

vapor depositing the alternating layers on the substrate to form the  
reactive multilayer foil; and

10 separating the multilayer foil from the substrate.

2. The method of claim 1 wherein the substrate has sufficient adherence  
to the deposited layers to retain the layers during deposition but insufficient  
adherence to prevent removal of the multilayer foil after deposition.

15

3. The method of claim 1 wherein the layers comprise one or more  
layers of aluminum, and at least one of the layers of aluminum is deposited in  
contact with the substrate.

20

4. The method of claim 3 wherein the substrate comprises silicon.

5. The method of claim 1 wherein the substrate comprises a coating of a release material or a coating of an adhesion material.

6. The method of claim 1 wherein the substrate comprises a removable 5 sacrificial layer.

7. The method of claim 1 wherein the substrate comprises a removable sacrificial layer of copper, brass or photoresist.

10 8. The method of claim 1 wherein the vapor depositing comprises physical vapor deposition.

9. The method of claim 8 wherein the vapor depositing comprises magnetron sputtering or electron beam evaporation.

15

10. The method of claim 1 wherein the substrate is cooled during the vapor depositing.

11. The method of claim 1 wherein the layers are deposited to form a multilayer foil having a thickness in the range 50 $\mu$ m-1cm.

12. The method of claim 1 wherein the vapor depositing is under 5 conditions chosen to minimize stress in the deposited layers.

13. A method of bonding a first body to a second body comprising the steps of:

disposing between the first body and the second body, a freestanding 10 reactive multilayer foil;  
pressing the bodies together against the foil; and  
igniting the reactive foil.

14. The method of claim 13 wherein at least one of the bodies is a 15 semiconductor or microelectronic device.

15. The method of claim 13 wherein the reactive multilayer foil has a thickness in excess of 10 $\mu$ m.

16. The method of claim 13 wherein the bodies have coefficients of thermal expansion differing by at least 1  $\mu\text{m}/\text{m}/^\circ\text{C}$ .

5 17. The method of claim 13 wherein the first body comprises metal and the second body comprises ceramic material.

18. The product made by the method of claim 13.

10 19. A reactive multilayer foil comprising:

a foil composed of alternating layers that react exothermically, wherein the foil includes a plurality of openings through the foil.

20. A reactive multilayer foil according to claim 19 wherein the  
15 openings are filled with meltable material, propellant, or material that changes or reacts on heating.

21. A reactive multilayer foil according to claim 19 wherein the openings are periodically arranged across the area of the foil.
22. A method of making a reactive multilayer foil comprising the steps of:
  - 5 providing a substrate having a surface including a plurality of preformed openings, bumps, or particles of thickness or depth similar to or greater than the multilayer foil to be deposited;
  - depositing on the surface a plurality of layers to form the reactive multilayer foil; and
  - 10 separating the multilayer foil from the substrate.

23. A method of making a reactive multilayer foil comprising the steps of:
  - 15 providing a flat substrate;
  - depositing on the substrate a plurality of layers to form a reactive multilayer foil;
  - depositing a masking layer on top of the reactive foil;
  - patterning the masking layer with a plurality of holes;
  - etching the reactive foil through the holes; and

separating the multilayer foil from the substrate.

24. A method of making a reactive multilayer foil comprising the steps of:

5 providing a flat substrate;

depositing on the substrate a plurality of layers to form a reactive multilayer foil; and

mechanically pressing a plurality of holes into the reactive foil.

10 25. A method of making a reactive multilayer foil comprising the steps of:

making a reactive multilayer foil having a plurality of openings through the foil, and

15 filling the openings in the multilayer foil with meltable material, propellant, or material that will change or react on heating when the reactive foil is ignited.

26. A method of bonding a first body to a second body comprising the steps of:

disposing between the first body and the second body, a reactive multilayer foil and at least one melttable joining material, the reactive multilayer foil having a plurality of openings through the thickness of the foil;

pressing the bodies together against the foil and the joining material; and

5 igniting the reactive foil to melt the joining material and permit the melted material to flow through the openings to join the first and second bodies.

27. The method of claim 26 wherein at least one of first body or the

second body comprise a semiconductor or a microelectronic device.

10 28. The method of claim 26 wherein the first body and the second body  
have CTEs that differ by more than about  $1\mu\text{m}/\text{m}^{\circ}\text{C}$ .

29. The product made by the method of claim 26.

15 30. The product made by the method of claim 27.

31. The product made by the method of claim 28.

32. A composite reactive multilayer foil comprising:

at least one first set of reactive layers; and

at least one second set of reactive layers in thermal contact with the first set, the layers of the first set having thicknesses which are relatively larger than 5 those of the second set, whereby the layers of the second set, upon ignition, ignite the thicker layers of the first set.

33. A composite reactive multilayer foil comprising:

a first set of reactive layers; and

10 a second set of reactive layers in thermal contact with the first set, the layers of the first set having compositions which are relatively more reactive than the second set, whereby the layers of the first set, upon ignition, ignite the less reactive layers of the second set.

34. A reactive multilayer foil comprising:

15 a multilayer foil having an area composed of at least two different regions, one or more first regions composed of layers that can react exothermically to form electrically conductive material and one or more second regions which are non-conductive or react to form non-conductive material.

35. A method of connecting a semiconductor or microelectronic device having one or more electrical contacts to a substrate having one or more receiving contacts, comprising the steps of:

disposing between the device and the substrate a reactive multilayer foil  
5 composed of one or more first regions that can react exothermically to form electrically conductive regions and one or more second regions which are non-conductive or react to form non-conductive material.;

registering the contacts of the device, the contacts of the substrate and the first regions of the foil,

10 pressing the device and the substrate together against the foil; and  
igniting the foil.

36. A method for bonding a first body to a second body comprising the steps of:

15 disposing between the first body and the second body, a reactive multilayer foil comprising a plurality of successive exothermic reactive layers that react to form a joining material;

pressing the bodies together against the foil; and  
igniting the foil.

37. The method of claim 36 wherein at least one of the first and second bodies comprise metallic glass.

5 38. The method of claim 37 wherein the reactive multilayer foil comprises alternate layers of alloys that, after reaction and cooling, are amorphous.

10 39. The method of claim 37 wherein the reactive multilayer foil comprises alternate layers of an alloy comprising Ni or Cu, an alloy comprising Ti, Zr, or Hf, and an alloy containing primarily Al.

40. A method of bonding a first body to a second comprising the steps of:

15 disposing between the first body and the second body, a freestanding reactive multilayer foil and at least one layer of melttable joining material;

pressing the bodies together against the foil and joining material; and

igniting the reactive foil to melt the joining material.

41. The method of claim 40 wherein the joining material is coated on the foil.

5 42. The method of claim 40 wherein the joining material is freestanding.

43. A bonded structure comprising:

a first body;

10 a second body bonded to the first body by a joining region, the joining region comprising a reacted multilayer structure including a periodic array of openings therethrough, the structure embedded in a matrix of melttable joining material extending through the openings to join the first body and the second body.

15

FIG. 1

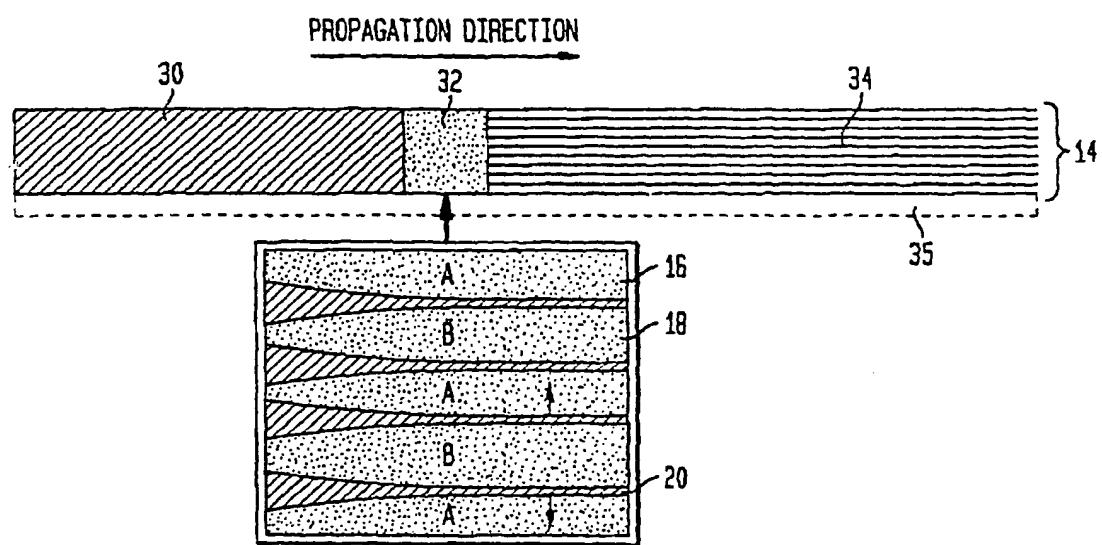


FIG. 2

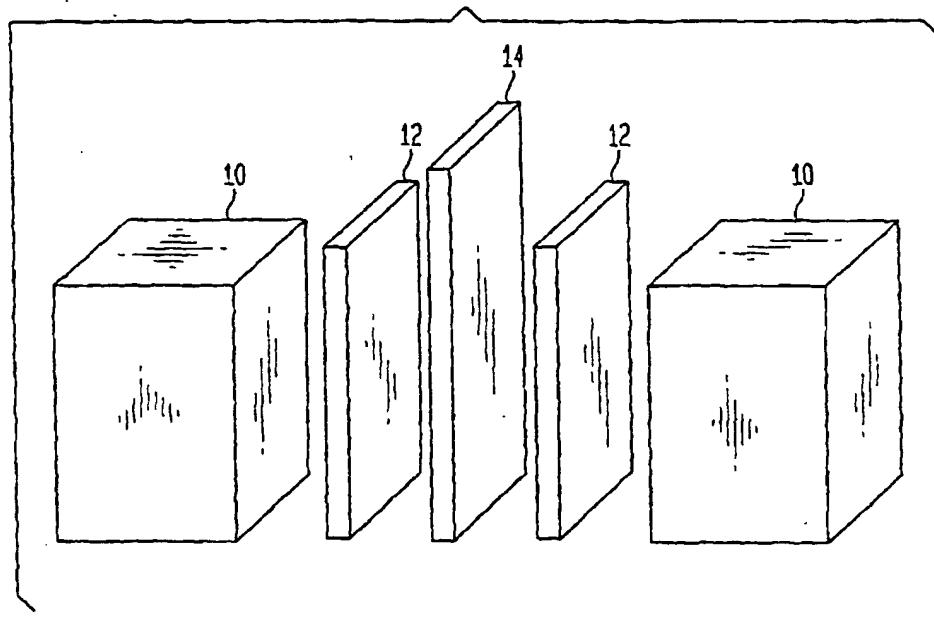


FIG. 3

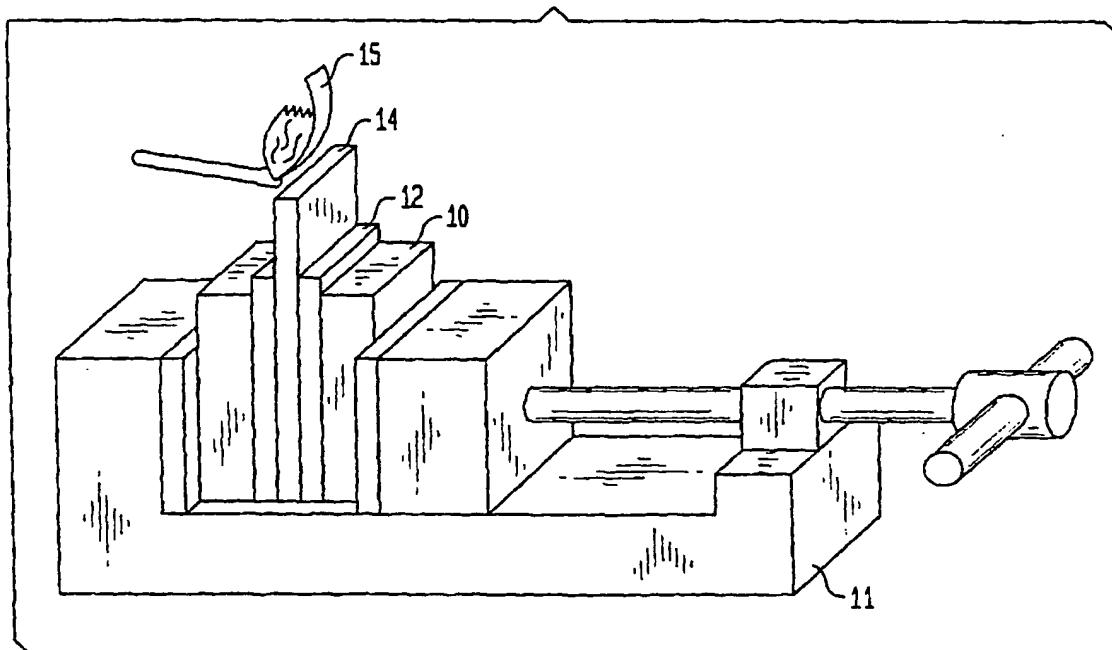


FIG. 4

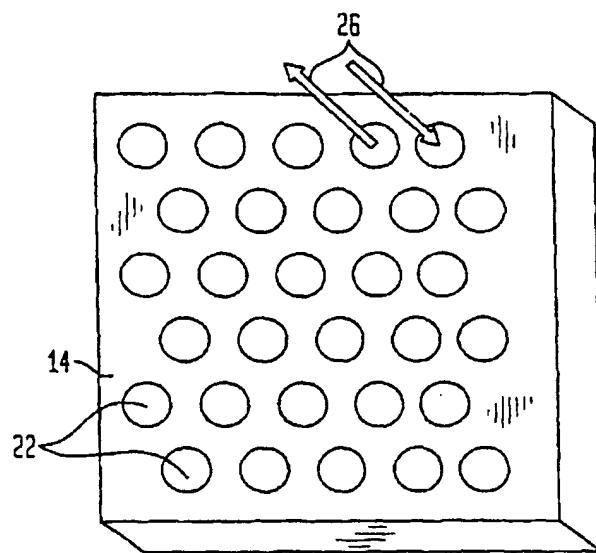


Fig. 5

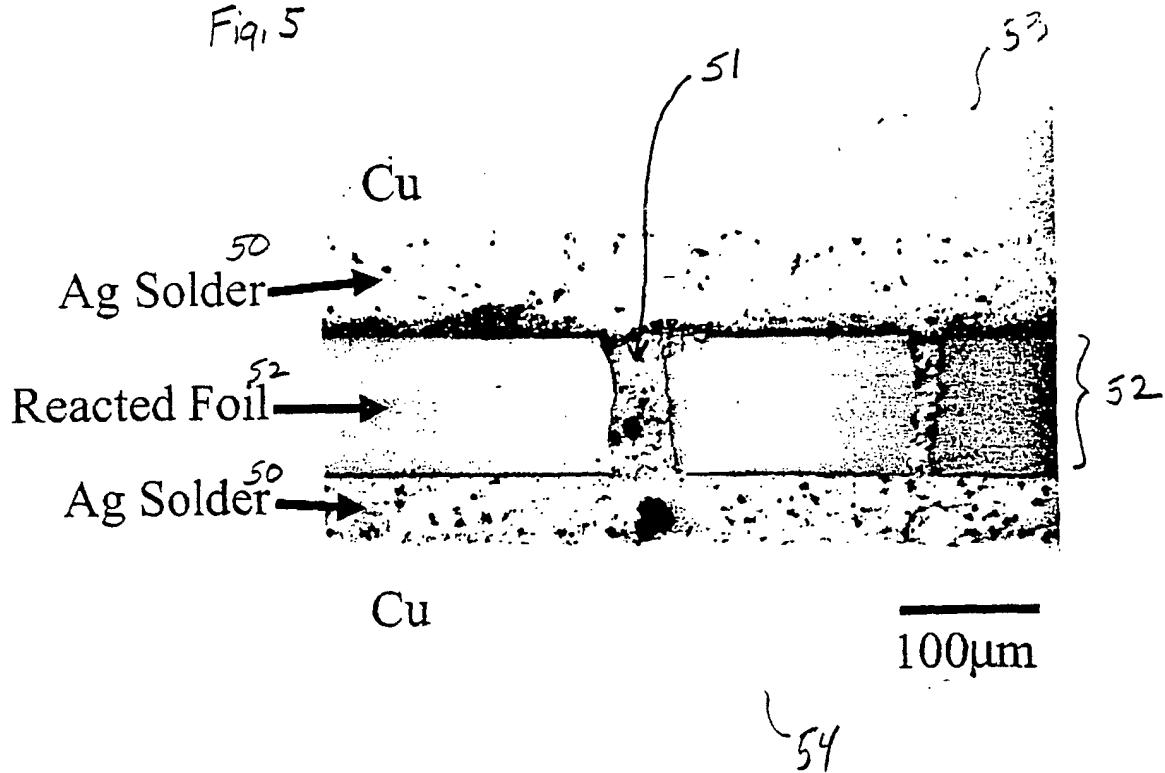


Fig. 6

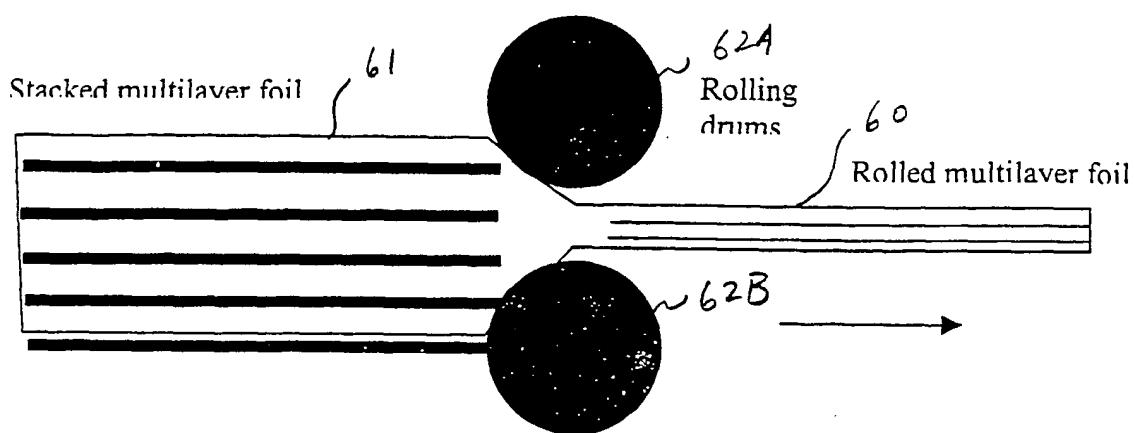


Fig. 8

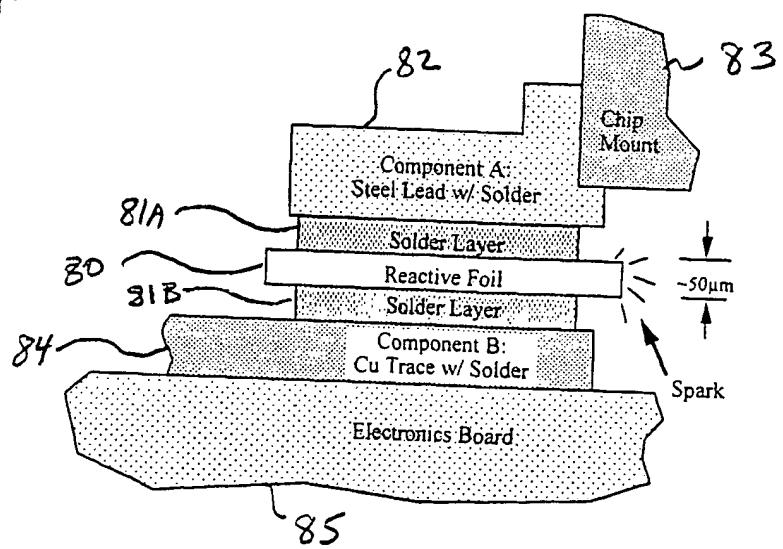


Fig. 7

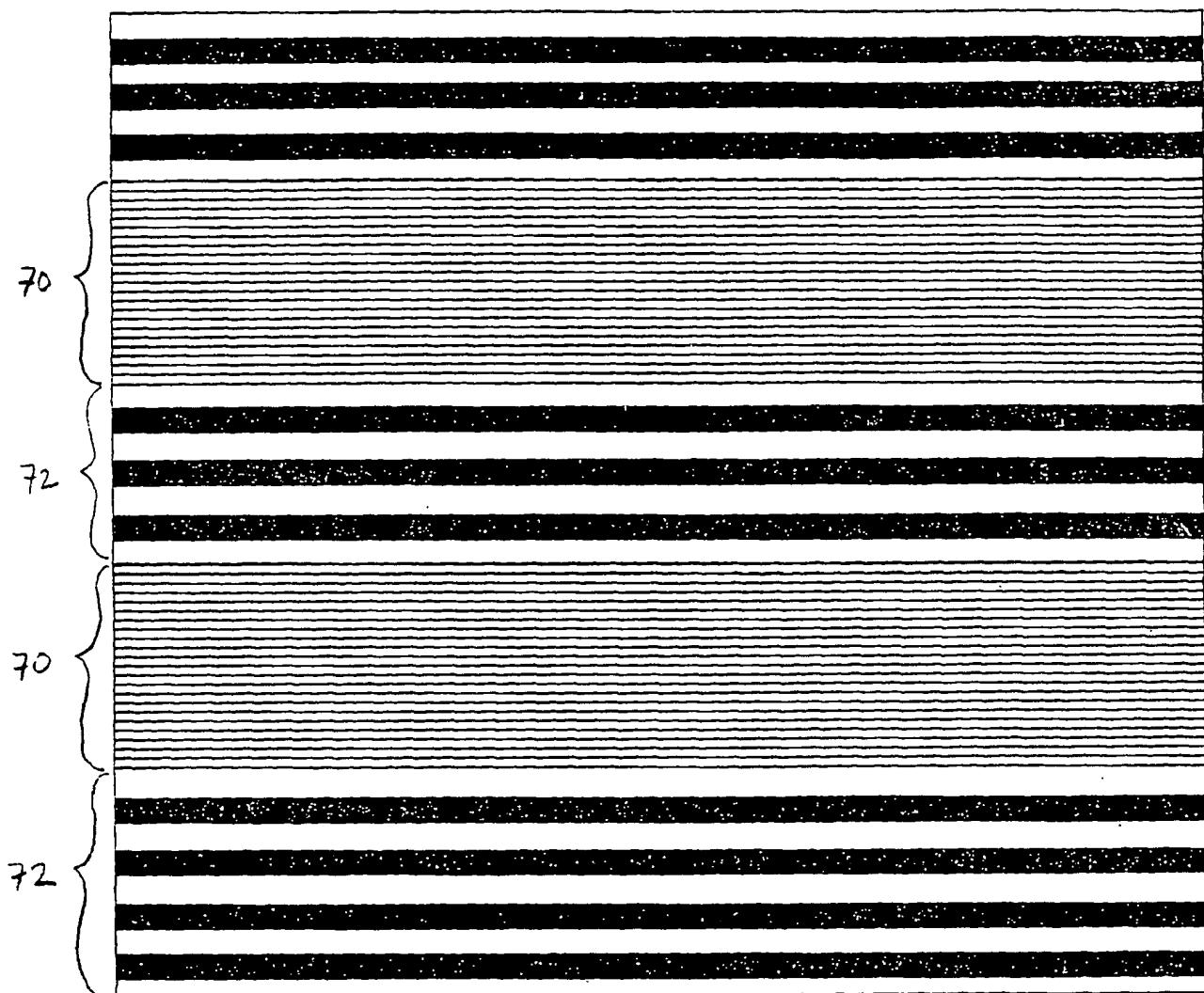
 $\frac{71}{7}$ 

Fig. 9A

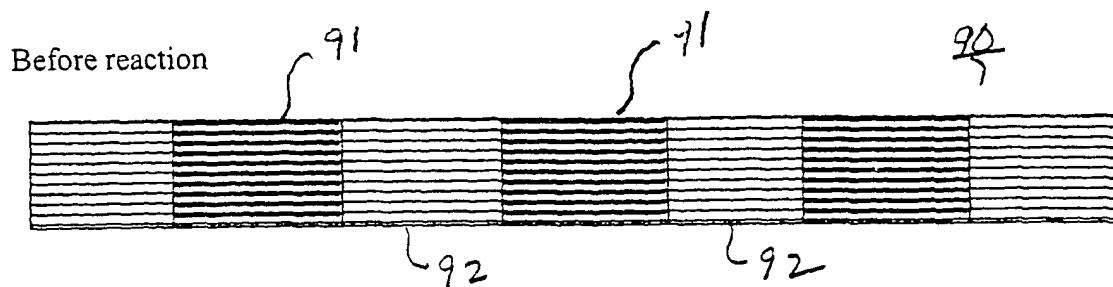
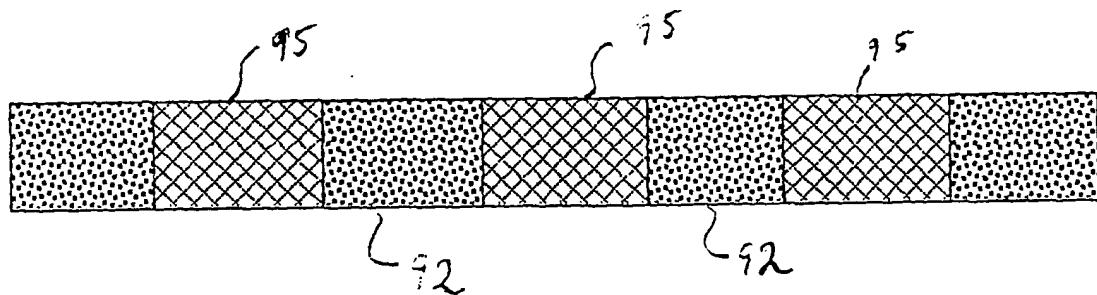


Fig. 9B

After reaction



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/14053

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

- I. Claims 1-12, drawn to a method of making a freestanding reactive multilayer foil.
- II. Claims 13-18, 26-31, and 35-43, drawn to a method of bonding a first body to a second body.
- III. Claims 19-21, drawn to a reactive multilayer foil.
- IV. Claim 22, drawn to a method of making a reactive multilayer foil.
- V. Claim 23, drawn to a method of making a reactive multilayer foil.
- VI. Claim 24, drawn to a method of making a reactive multilayer foil.
- VII. Claim 25, drawn to a method of making a reactive multilayer foil.
- VIII. Claim 32, drawn to a composite reactive multilayer foil.
- IX. Claim 33, drawn to a composite reactive multilayer foil.
- X. Claim 34, drawn to a composite reactive multilayer foil.

The inventions listed as Groups I-X do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: Group I deals with making a foil by vapor deposition of alternating layers; Group II deals with bonding first and second bodies by the steps of disposing a foil between the bodies, pressing the bodies against the foil, and igniting the foil; Group III deals with a foil with openings therein composed of exothermically reactive alternating layers; Group IV deals with making a foil by using a substrate having a surface including a plurality of preformed opening, bumps, or particles; Group V deals with making a foil by depositing a masking layer, patterning the masking layer with a plurality of holes, and etching the foil through the holes; Group VI deals with making a foil by mechanically pressing a plurality of holes into the foil; Group VII deals with making a foil by making holes in the foil and filling the holes with meltable material; Group VIII deals with a composite foil including the layers of the first set having thicknesses which are relatively larger than the layers of the second set; Group IX deals with a composite foil including the layers of the first set having compositions which are relatively more reactive than the layers of the second set; and Group X deals with a foil including at least two different regions wherein one or more of the first region is composed of layers that can react exothermically to form electrically conductive material and one or more of the second region is non-conductive or react to form non-conductive material.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/14053

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B29C; C06B 45/12  
 US CL : 149/14; 264/81, 154, 156, 255, 267, 299

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 149/14; 264/81, 154, 156, 255, 267, 299

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EAST

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,381,944 A (MAKOWIECKI et al) 17 January 1995 (17.01.1995) see entire document.	1-43
Y	US 5,773,748 A (MAKOWIECKI et al) 30 June 1998 (30.06.1998) see entire document	1-43
Y	US 5,266,132 A (DANEN et al) 30 November 1993 (30.11.1993) see entire document.	1-43
Y	US 5,490,911 A (MAKOWIECKI et al) 13 February 1996 (13.02.01996) see entire document.	1-43

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance
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"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search

10 September 2001 (10.09.2001)

Date of mailing of the international search report

09 OCT 2001

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231

Facsimile No. (703)305-3230

Authorized officer

EDMUND H LEE

Jean Proctor  
 Paralegal Specialist

Telephone No. 703.308.0661

Exhibit G

**PATENT APPLICATION TRANSMITTAL LETTER**  
(Small Entity)

Docket No.  
13631-2A

**TO THE ASSISTANT COMMISSIONER FOR PATENTS**

Transmitted herewith for filing under 35 U.S.C. 111 and 37 C.F.R. 1.53 is the patent application of:

**T.P. WEIHS, T. HUFNAGEL, O. KNIO, M. REISS, D. vanHEEDEN and H. FELDMESER**

For: **FREESTANDING REACTIVE MULTILAYER FOILS**

Enclosed are:

Certificate of Mailing with Express Mail Mailing Label No. **ET283689714US**

**SIX (6)** sheets of drawings.

A certified copy of a application.

Declaration  Signed.  Unsigned.

Power of Attorney

Information Disclosure Statement

Preliminary Amendment

**NOT REQUIRED** Verified Statement(s) to Establish Small Entity Status Under 37 C.F.R. 1.9 and 1.27.

Other: **ASSIGNMENT**

**CLAIMS AS FILED**

For	#Filed	#Allowed	#Extra	Rate	Fee
<b>Total Claims</b>	43	- 20 =	23	x \$9.00	\$207.00
<b>Indep. Claims</b>	15	- 3 =	12	x \$40.00	\$480.00
<b>Multiple Dependent Claims (check if applicable)</b>					\$0.00
				<b>BASIC FEE</b>	\$355.00
				<b>TOTAL FILING FEE</b>	\$1,042.00

A check in the amount of to cover the filing fee is enclosed.

The Commissioner is hereby authorized to charge and credit Deposit Account No. **510358** as described below. A duplicate copy of this sheet is enclosed.

Charge the amount of **\$1,042.00** as filing fee.

Credit any overpayment.

Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.

Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Dated: **05/01/2001**

  
*Glen E. Books*  
Signature

**GLEN E. BOOKS**  
REG. NO. 24, 950

**LOWENSTEIN SANDLER PC**  
**65 LIVINGSTON AVENUE**  
**ROSELAND, NJ 07068**  
**973-597-6162**

cc:

Exhibit #



# UNITED STATES PATENT AND TRADEMARK OFFICE

COMMISSIONER FOR PATENTS  
UNITED STATES PATENT AND TRADEMARK OFFICE  
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www.uspto.gov

APPLICATION NUMBER	FILING DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	DRAWINGS	TOT CLAIMS	IND CLAIMS
60/362,976	03/08/2002	80		13631-2 ?		6	

CONFIRMATION NO. 3190

28221  
GLEN E. BOOKS, ESQ.  
LOWENSTEIN SANDLER PC  
65 LIVINGSTON AVENUE  
ROSELAND, NJ 07068

## FILING RECEIPT



\*OC00000008014954\*

Date Mailed: 05/02/2002

Receipt is acknowledged of this provisional Patent Application. It will not be examined for patentability and will become abandoned not later than twelve months after its filing date. Be sure to provide the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION when inquiring about this application. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please write to the Office of Initial Patent Examination's Filing Receipt Corrections, facsimile number 703-746-9195. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections (if appropriate).

### Applicant(s)

Timothy P. Weihs, Baltimore, MD;  
Todd Hufnagel, Baltimore, MD;  
Omar Knio, Timonium, MD;  
Michael Reiss, Baltimore, MD;  
David van Heerden, Baltimore, MD;  
Howard Feldmesser, Columbia, MD;

If Required, Foreign Filing License Granted 05/02/2002

Projected Publication Date: Not Applicable

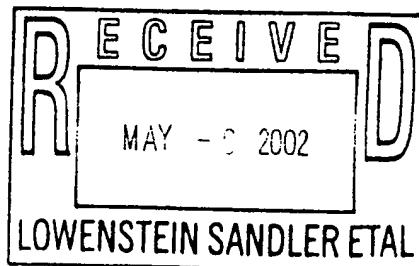
Non-Publication Request: No

Early Publication Request: No

\*\* SMALL ENTITY \*\*

### Title

Freestanding reactive multilayer foils



### LICENSE FOR FOREIGN FILING UNDER

**Title**

Freestanding reactive multilayer foils

**Preliminary Class**

428

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**Data entry by :** BEYENE, MELKAM

**Team :** OIPE

**Date:** 06/27/2001



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Title 37, Code of Federal Regulations, 5.11 & 5.15**

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1/6

FIG. 1

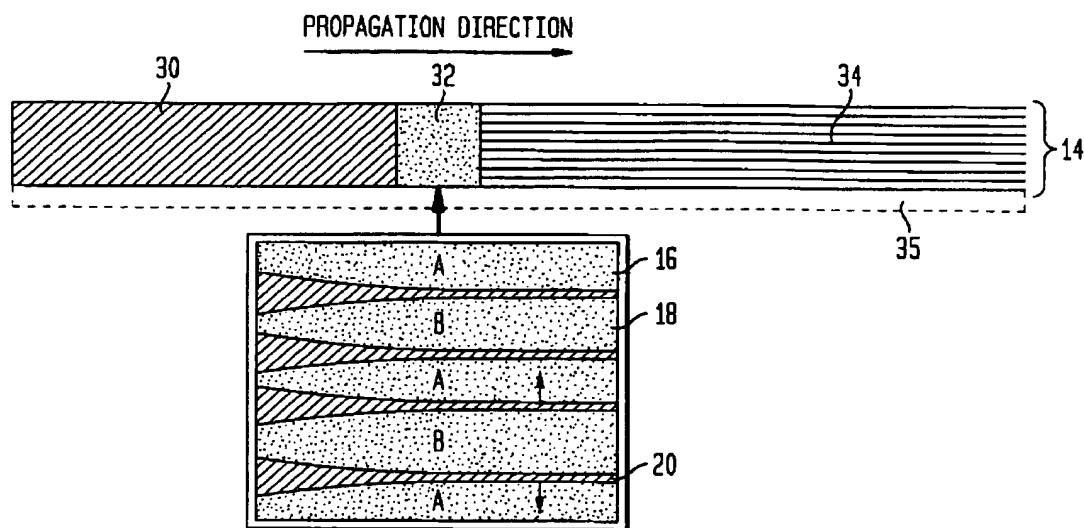
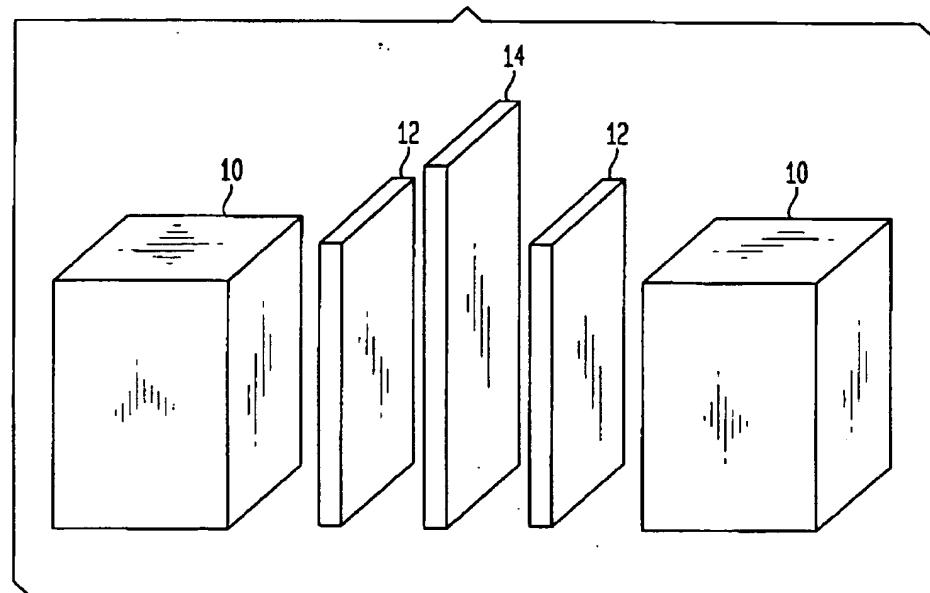


FIG. 2



2/6

FIG. 3

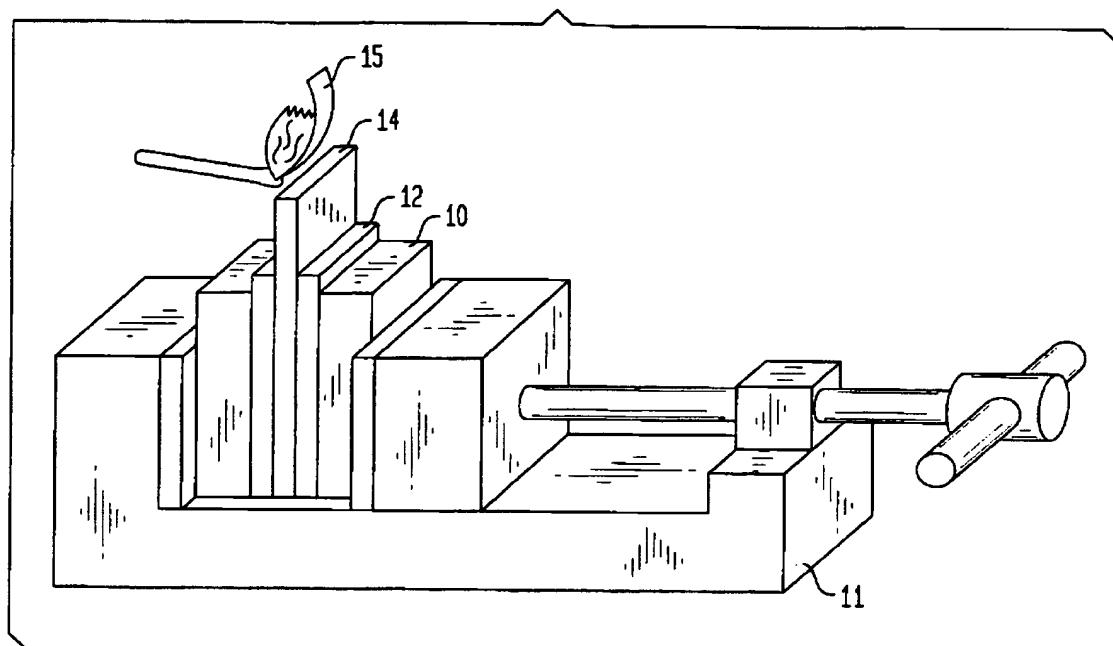
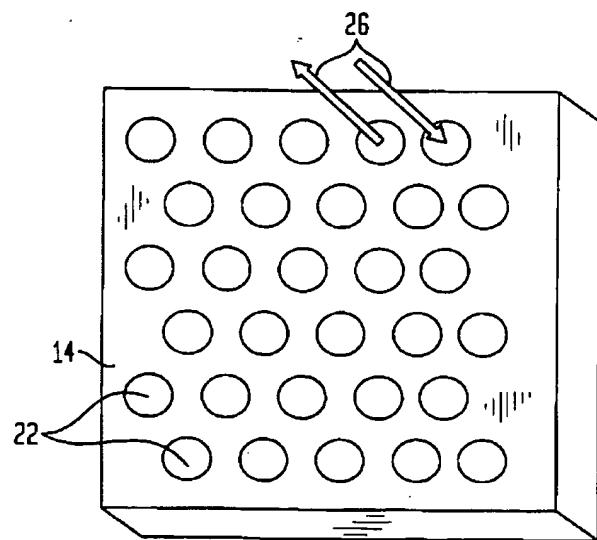


FIG. 4



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P. 004

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*FIG. 5*

4/6

FIG. 6

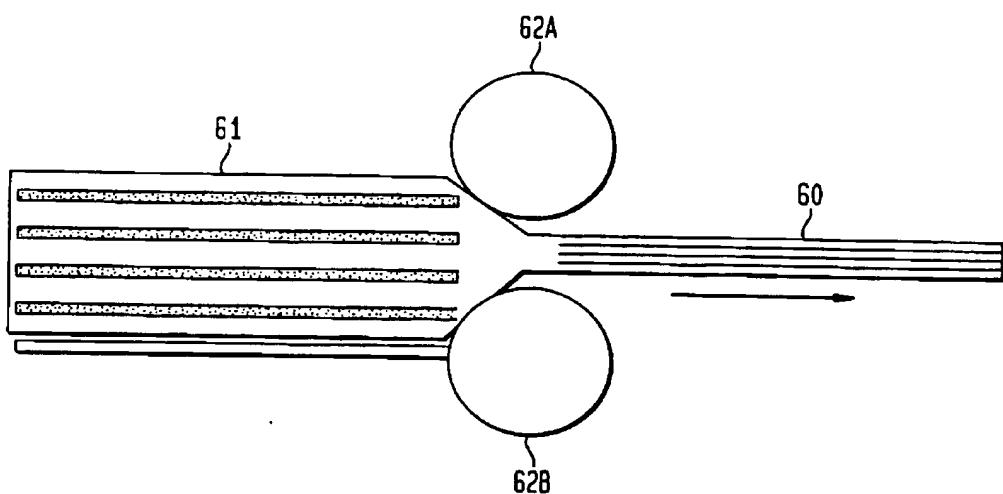
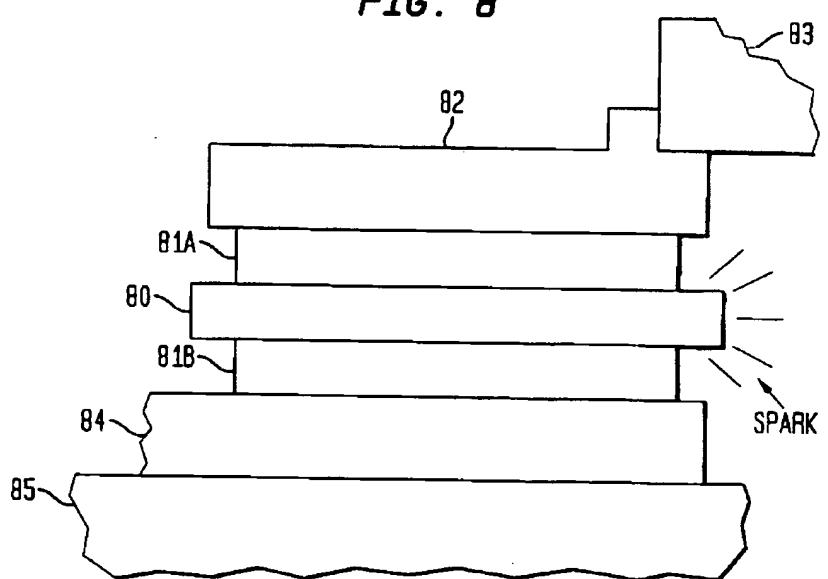


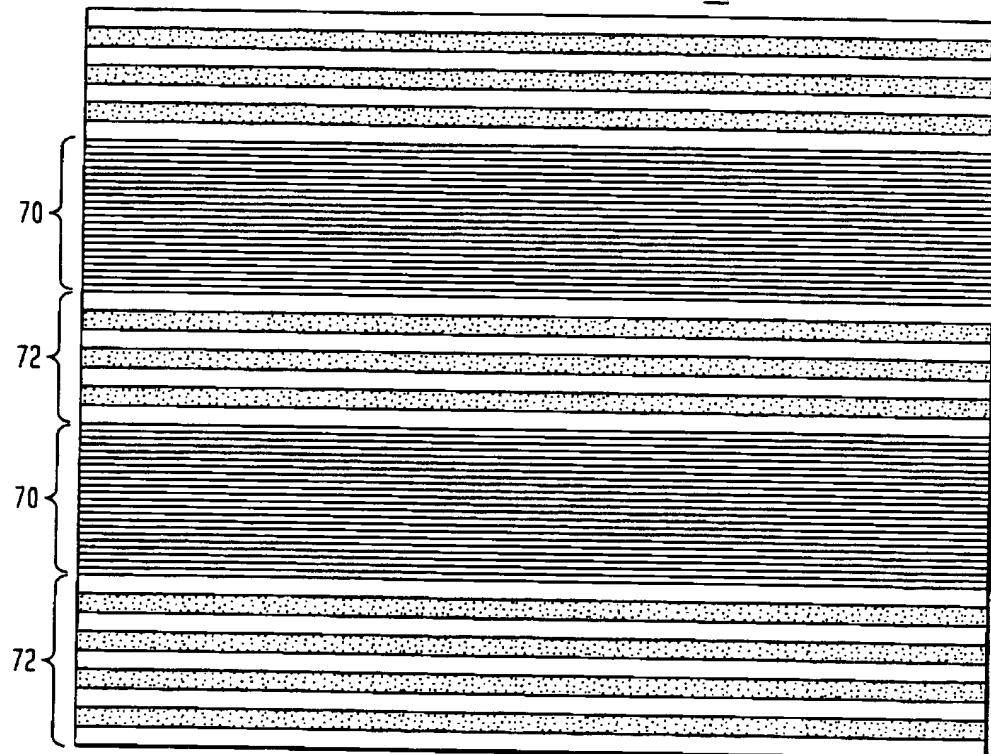
FIG. 8



5/6

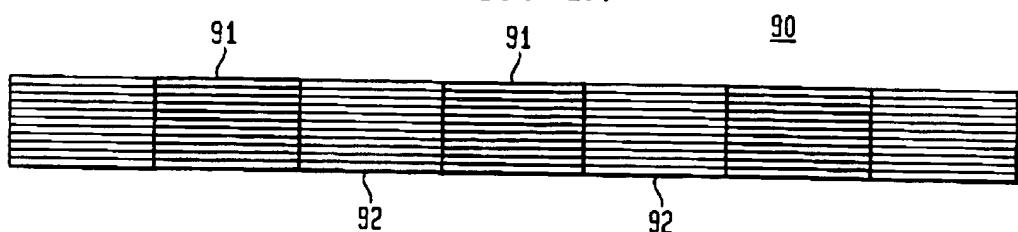
FIG. 7

71

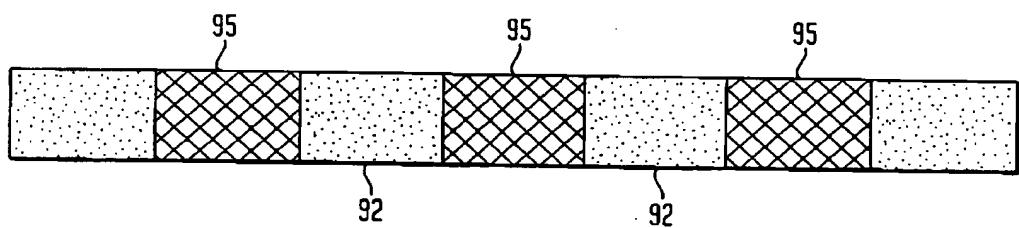


6/6

*FIG. 9A*



*FIG. 9B*



LOWENSTEIN SANDLER PC

*Attorneys at Law*

GLEN E. BOOKS  
Member of the Firm

Tel 973.597.6162 Fax 973.597.6163  
[gbooks@lowenstein.com](mailto:gbooks@lowenstein.com)

July 2, 2001

**VIA FIRST CLASS MAIL**

Dr. Timothy P. Weihs  
Dept. of Materials Science and Engineering  
John Hopkins University  
102 Maryland Hall  
3400 N. Charles Street  
Baltimore, MD 21218

Dear Dr. Weihs:

Enclosed please find a copy of the Official Filing Receipt received in connection with your case entitled: "FREESTANDING REACTIVE MULTILAYER FOILS."

We will keep you apprised of further developments. Also, if you want these reporting items to go to someone else just drop me an e-mail instructing as to who should receive them. Thank you.

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